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Technical Progress Report 65-2, Annual

March 15, 1964 to March 14, 1965

SENSITIVITY FUNDAMENTALS (U)

Prepared for:

OFFICE OF NAVAL RESEARCH
DEPARTMENT OF THE NAVY
WASHINGTON 25, D.C.

CONTRACT NO. Nonr 3760(00)

Sponsored by: ARPA - PROPELLANTS CHEMISTRY OFFICE
ARPA ORDER NO. 301, AMENDMENT NO. 3





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ABSTRACT

Under the sponsorship of ARPA and the Office of Naval Research, Stanford Research Institute is studying fundamental sensitivity properties of difluoroamino compounds in the following situations:

1. The detonation characteristics including the shock sensitivity of the liquid phase
2. The relation of shock sensitivity and failure diameter to the flow and the chemical reaction rate behind the shock front
3. The mechanism and kinetics of thermal decomposition of the compounds in solution and in the liquid phase.

These interrelated situations were chosen for their susceptibility to analysis in terms of basic physical and chemical parameters. Each study is being carried out on 1,2-bis(difluoroamino)propane (1,2-DP) and 2,2-bis(difluoroamino)propane (2,2-DP), in order to assess the importance of structural variation. Thermal decomposition studies have also begun on 1,3-bis(difluoroamino)propane (1,3-DP).

A. Detonation Sensitivity. The shock sensitivities of 2,2-DP and IBA have been measured. The 2,2-DP sensitivity was found to be 13.2 ± 0.5 mm of Plexiglas in lead cups (9.5 mm I.D. x 2 mm wall). The IBA sensitivity was measured in lead cups (20 mm I.D. x 2 mm wall) and found to be 14.4 ± 0.2 mm of Plexiglas. The effect of the detonation sensor, a continuous wire mounted in a holder, was investigated. It was concluded that a wire reaching to the donor-acceptor interface can cause an apparent increase in sensitivity, but a wire reaching halfway into the test liquid does not affect the sensitivity for the charge length used. From streak camera photographs of the sensitivity test, it appears that initiation occurs at the tube walls. There may also be an initiation effect, as yet unexplained, caused by the type of material which seals the test cup bottom. The donor-attenuator calibration has been checked and a large amount of scatter was noted, probably caused by irreproducibility of the donor components.

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B. Low Velocity Reaction Waves. Low velocity reaction waves have been observed in a mixture of 90% (by weight) nitromethane - 10% tetranitromethane in steel tubes 25.4 mm I.D. x 6.35 mm wall. The average velocity in the liquid is 1.5 mm/ μ sec and the average recorded shock pressure about 13 kbars. By observing this mixture in sample containers of CR-39 and of aluminum, steel, and lead, all equipped with windows made of CR-39, the precursor wave in the sample container walls and the slower reaction wave in the liquid mixture has been seen. The average velocity in the liquid is 1.5 ± 0.4 mm/ μ sec and is independent of container material.

C. Detonation at Low Temperatures. Two methods for determining the detonation velocity have been successfully adapted to distinguish between detonating and nondetonating phenomena at cryogenic temperatures. The methods are (1) the modified Dautriche method which compares the detonation velocity of a known explosive with that of the test material, and (2) the continuous resistance wire method. Both methods confirm that liquid perfluorohydrazine does not detonate under the test conditions.

D. Failure Diameter and Reaction Time. The failure diameter for a Chapman-Jouguet detonation wave in 1,2-DP in massive lead confinement is between 1.6 and 2.0 mm. Failure diameter determinations for 2,2-DP and IBA are partially completed. The detonation velocity of 1,2-DP was measured as 5.89 ± 0.05 mm/ μ sec at 37°C with the liquid confined in a 25 mm I.D. by 6.3 mm CR-39 plastic tube. Hugoniot curves are being determined for Plexiglas, CR-39, nitromethane, and difluoroamino compounds. Preliminary measurements have been made of the reaction time of nitromethane as a function of Plexiglas attenuator thickness. Methods for the measurement of reaction times in difluoroamino compounds are being refined.

E. Low Pressure Pyrolysis. The thermal decomposition of 1,2-DP and 2,2-DP has been studied by passage of small quantities of the compounds into a heated quartz vessel at pressures so low that only gas-wall collisions occur. Products emerging by diffusion were analyzed by a mass spectrometer. Results of preliminary observations of 1,2-DP and 2,2-DP decomposed at 600-900°C show that (a) 2,2-DP decomposes faster than 1,2-DP

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in our system; (b) decomposition of 1,2-DP gives as one of the major reaction paths: $C_3H_6 + 2NF_3$; (c) most of the main features of the 1,2-DP decomposition can be accounted for by assuming an initial NF_3 split out, followed by rearrangement; (d) under these conditions there seems to be no need to propose a homogeneous HF elimination for either 1,2-DP or 2,2-DP; and (e) there is no evidence for catalytic decomposition of either compound on the quartz walls.

F. Decomposition of NF Compounds in Solution. Early studies suggested that the thermal decomposition of NF compounds proceeded through a dehydrofluorination catalyzed by acid, base, or both. Studies during this report period in 10% dioxane-water at 50° with 1,2-DP show that there is no acceleration of decomposition by addition of HCl and thus, at least under these conditions, no acid catalysis. The dehydrofluorination of NF compounds is most likely promoted by water, acting as a base in the elimination reaction. Experiments in methanol-d show that the elimination is probably a concerted one.

Studies with 2,2-DP indicate that for these same conditions it is completely stable. The 1,3 isomer, from a qualitative study, decomposes more slowly than does 1,2-DP. Furthermore 1,2-DP and 1,3-DP readily undergo dehydrofluorination in the presence of base.

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I INTRODUCTION

The word sensitivity implies a quantitative measure of the ease of inducing in a material a rapid exothermic chemical decomposition accompanied by a pressure rise of sufficient magnitude to be destructive. Many empirical tests devised to measure sensitivity fail to correlate, are only partially satisfactory as predictive tests, and give little fundamental information. Moreover, the results of such tests are not interpretable in terms of basic physical and chemical behavior.

There are two reasons for this unsatisfactory state of affairs. First, many of the tests are so complicated that they cannot be reduced to the basic physics and chemistry of the system. From the results, one cannot analyze the physical events reliably enough to deduce the chemistry; nor does one know the chemistry well enough to be able to interpret the results in terms of the applied disturbance. Second, there are several different kinds of events the results of which can be termed explosive. For example, a given high energy liquid chemical, depending upon circumstances and upon its chemical and physical characteristics, may undergo one or more of the following kinds of exothermic reaction accompanied by a very fast pressure rise: a detonation wave in the liquid phase; thermal decomposition in the liquid phase uniformly throughout the mass; vaporization of the liquid, followed by a detonation wave in the gas phase; vaporization of the liquid, followed by thermal decomposition in the gas phase; vaporization of the liquid, followed by initiation of a deflagration wave in the gas phase, and then by ignition and deflagration in the liquid phase.

The reason for the lack of correlation of the empirical sensitivity tests may often be that the tests are concerned with different events in the lists above, i.e., different paths of decomposition. A card-gap test presumably measures sensitivity to detonation of the liquid phase. A drop-weight or impact test may reflect, at least in part, the ease of thermal decomposition of the liquid phase, i.e., ignitability. The hot-wire test may measure the ease with which the liquid vaporizes and ignites in the vapor phase. Ignition in vapor phase may be reflected by

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the adiabatic compression test. Thermal stability measurements may reflect liquid phase decomposition kinetics.

Clearly, it is desirable to define precisely the event during any sensitivity measurement. In order to predict with assurance the kind of explosive behavior to be expected of a material under a given set of circumstances, one should know:

1. Thermal stability in terms of liquid phase decomposition kinetics
2. Detonability of liquid phase, i.e., whether it will support a detonation wave, and the failure diameter for detonation
3. The necessary conditions for initiating a detonation wave in the liquid phase
4. Deflagrability of the liquid phase, i.e., the conditions of pressure and geometry, if any, under which the liquid supports a deflagration wave at its surface
5. The necessary conditions for initiating a deflagration wave at the liquid surface
6. The decomposition kinetics of the vapor phase
7. Detonability of the vapor phase
8. The necessary conditions for initiating a detonation wave in the vapor phase
9. Deflagrability of the vapor phase
10. The necessary conditions for initiating a deflagration wave in the vapor phase.

In this work we have been primarily concerned with obtaining experimental information for simple NF compounds which relates to the first three decomposition paths listed above. A part of the effort to obtain quantitative data on the critical diameter for detonation, detonation velocity, and detonation sensitivity of selected liquid propellants. In addition, thermal decomposition kinetics and mechanisms, and their relationship to detonation phenomena are being studied to obtain a more complete understanding of the decomposition paths available to an exploding liquid. We

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expect the information on decomposition kinetics to be useful in understanding and predicting sensitivity in other experimental situations.

The program is divided into three interrelated parts:

1. Detonation studies of liquid difluoroamino compounds
2. A study of the relation of shock sensitivity and failure diameter to the flow and chemical reaction rate behind the shock front
3. The mechanism and kinetics of thermal decomposition of difluoroamino compounds.

The detonation studies (1) include (a) measurement of the shock sensitivity of the difluoroamino compounds of interest; (b) determination of whether or not the compounds exhibit low-order detonation and, if so, the necessary conditions for initiation; (c) modification of the JANAF sensitivity test so that it will be more meaningful and more adaptable to conditions of extreme temperature and pressure.

The ultimate objective of the physics and chemistry of detonation, (2) above, is to relate initiation and failure behavior to decomposition kinetics. This involves: (a) demonstration of steady detonation of difluoroamino liquids; (b) measurement of detonation velocities; (c) calculation of detonation properties; (d) measurement of failure diameters; (e) study of events in the liquids as shocks of various magnitudes enter; (f) measurement of reaction times at pressures and temperatures comparable to those encountered in initiating shocks; (g) study, where possible, of the equation of state of the unreacted materials and the divergence of the reactive material in the wave. Part (3), in addition to providing rate data for the models of detonation behavior, will provide information for understanding the relationship between chemical structure and sensitivity.

The compounds chosen for this study are as simple as possible structurally and at the same time have physical properties which permit their use in each phase of the study. The model compounds are the

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bis(difluoroamino) isomers of the propane series, primarily 1,2- and 2,2-bis(difluoroamino)propane (1,2- and 2,2-DP) and 1,2-bis(difluoroamino)-2-methyl propane (IBA). These compounds are being used so that the information from each experimental technique can be interrelated without having to account for differences in compounds, such as functional groups, carbon content, and chain branching. By employing isomers, structural effects on the results in a particular technique can be determined--for example, the differences between vicinal and geminate difluoroamino groups, and their position on the carbon chain.

The previous quarterly report reviewed and discussed the experimental information obtained with respect to detonability, low velocity reaction waves, and decomposition kinetics of several bis(difluoroamino)propane isomers and IBA, and the development of a booster test method for low temperature application.

This Third Annual Report emphasizes the most recent work on the modified JANAF sensitivity test, and the recent results from studies of detonation sensitivity calibration, failure diameter, low velocity reaction waves, and decomposition of 1,2- and 2,2-bis(difluoroamino)propane (1,2- and 2,2-DP) and 1,2-bis(difluoroamino)-2-methyl propane (IBA).

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II DETONATION SENSITIVITY

A. Introduction

During the past year the shock sensitivities of 2,2-DP and of IBA have been determined. The effects of the detonation sensor and of charge diameter on apparent sensitivity and the method of initiation in the sensitivity test have been investigated. The donor-attenuator calibration used for the shock sensitivity test has been checked.

B. Background

The description of the gap test used to determine shock sensitivity has been published in previous reports.¹ The CRISP apparatus² and witness plates were used to detect detonation.

C. Experimental Procedures and Results

1. Sensitivity Measurements

The failure diameter of 2,2-DP was found to be less than 5 mm in lead cups of 1 mm wall; the sensitivity was measured in 9.5 mm I.D. lead cups with 2 mm wall. The measured sensitivity is 13.2 ± 0.5 mm.

The failure diameter of IBA was found to lie between 10 and 15 mm in 2 mm wall lead cups and the sensitivity was measured in 20 mm I.D. x 2 mm wall lead cups. The measured sensitivity of IBA is 14.4 ± 0.2 mm. Table I summarizes the sensitivities of nitromethane, 1,2-DP, 2,2-DP, and IBA.

The sensitivities are not being reported in terms of pressure for the following reasons: (1) It seems probable from Seely's work³ that

¹Technical Progress Report 64-2, Annual, March 15, 1963 to March 14, 1964.

²A. B. Amster, P. A. Kendall, L. J. Veillette, and B. Harrell, Rev. Sci. Instr. 31, 188 (1960).

³Technical Progress Report 65-1, Quarterly, September 16 to December 15, 1964, Sect. V-C.

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Table I

LIQUID SENSITIVITIES

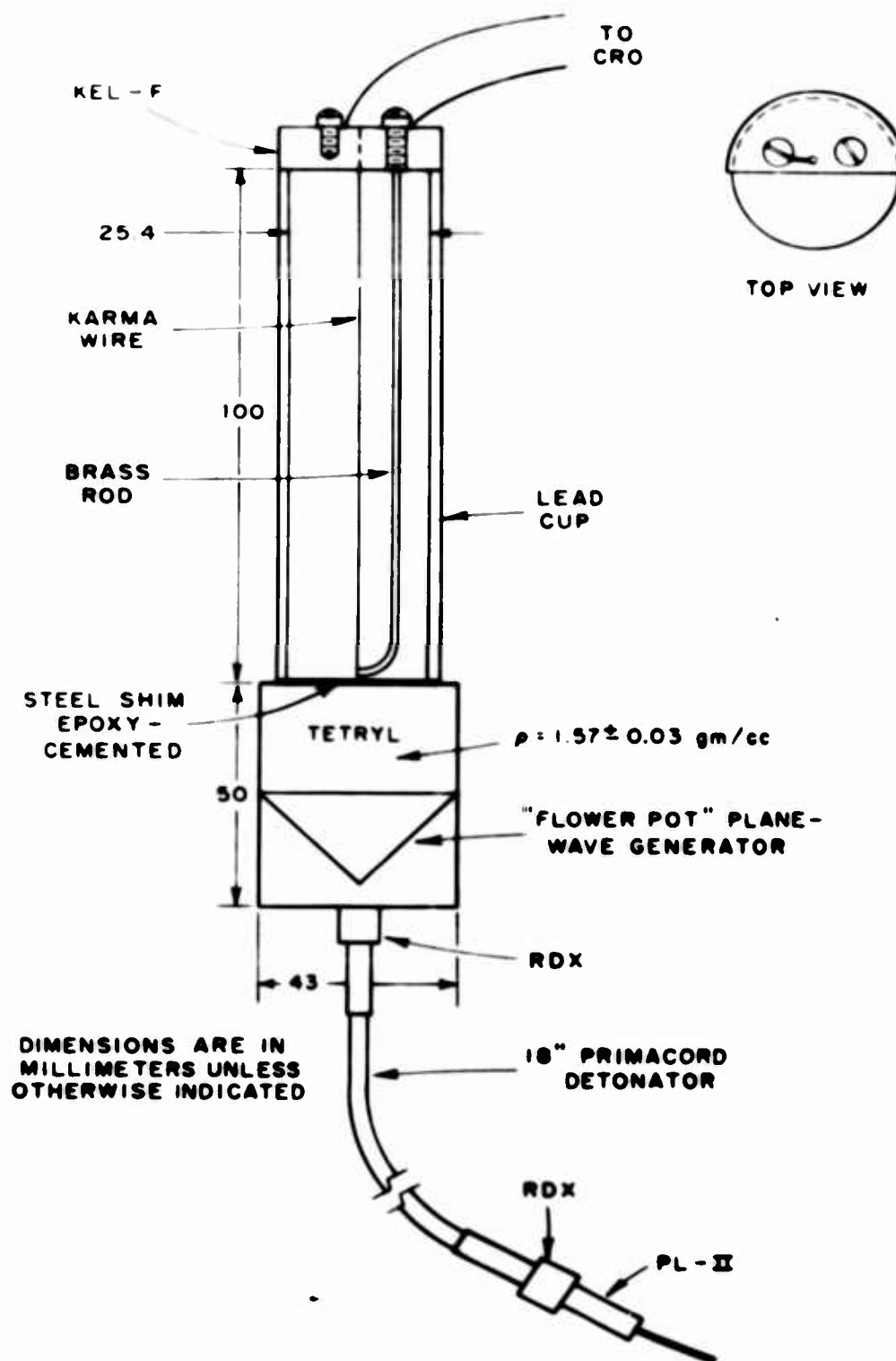
Liquid	Sensitivity	Confinement-Lead Tubes	
	Attenuator (mm)	I.D. (mm)	Wall Thickness (mm)
Nitromethane	11.1 ± 0.8	25.4	3.1
1,2-DP	15.8 ± 0.6	See Table III	
2,2-DP	13.2 ± 0.5	9.5	2
IBA	14.4 ± 0.2	20	2

the magnitude of the axial shock at the 50% point is lower than that required to cause homogeneous initiation. Initiation near the 50% point appears to be caused by shock interaction with the container walls and thus is not simply a function of the axial shock magnitude. (2) The 50% gap thickness is much more reproducible than the 50% pressure. The reason for this is not known, but the precision of the 50% point thickness suggests highly reproducible pressures for a given thickness which are not borne out by the pressure versus thickness calibrations. This is illustrated later in Figs. 3 and 4.

The effect on apparent sensitivity of using a CRISP wire mounted on a holder (Fig. 1) was investigated; two lengths of sensors, one that ran the entire length of the tube and the other only half way to the donor were employed. The liquids used were nitromethane and 1,2-DP. The results for nitromethane are given in Table II. The half-length wire and the witness plate give the same results, which differ significantly from those obtained using the full-length wire. Because of shock interaction with the full-length wire a weaker incident shock in this configuration is as effective as a stronger shock in the absence of the sensor. For 1,2-DP the full-length wire, the half-length wire, and the witness plate give essentially the same sensitivities. The assumption that a half-length wire will cause no spurious initiation in the general case is not completely justified, however. Consider, for example, a low velocity

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FIG. 1 SENSITIVITY TESTING WITH CONTINUOUS WIRE

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Table II

EFFECT OF SENSOR UPON APPARENT SENSITIVITY

Liquid: Nitromethane	
Confinement: Lead cups, 25.4 mm I.D. x 3.1 mm wall x 100 mm long	
Donor: Plane Wave Generator + 1 tetryl pellet	
Sensor	Sensitivity
	Attenuator (mm)
Full-length wire	16.1 \pm 0.4
Full-length wire	11.8 \pm 0.4
Witness plate	12.1 \pm 0.4

wave, such as reported by Van Dolah⁴ and others. Even at a considerable distance from a shock source such a wave might undergo a transition to a high velocity detonation upon interacting with an inhomogeneity. However, Mason reports⁵ several experiments in which wire sensors have been used as detectors of low velocity waves, and in no case did the wire cause a transition to a high velocity wave. We have repeated these experiments with similar results. Therefore, we feel that sensitivity tests conducted with a half-length sensor give valid results. Consequently, all sensitivities reported herein have been obtained using the half-length wire, unless otherwise noted.

The sensitivities we have measured have, in all cases, been at diameters greater than 1-1/2 times the failure diameter, for at such diameters the sensitivity has a maximum value. To confirm that the choice of test diameter is consistent with the goal (for safety) of reporting the maximum sensitivity, we have repeated tests on 1,2-DP using other diameters. The results are summarized in Table III where the average

⁴ R. W. Van Dolah, R. W. Watson, F. C. Gibson, C. M. Mason, and J. Ribovich, "Low Velocity Detonation in Liquid Explosives," Proc. International Conference on Sensitivity and Hazards of Explosives, London - October 1963 (Ministry of Aviation).

⁵ C. Mason, U.S. Bureau of Mines, Private Communication.

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Table III

EFFECT OF CHARGE DIAMETER UPON SENSITIVITY

Compound:		1,2-DP	
Confinement:		Lead cups	
Donor:		Plane wave generator + 1 tetryl pellet	
Sensor:		Half-length CRISP wire sensor	
Cup Dimensions (mm)			Sensitivity
I. D.	Wall	Length	Attenuator (mm)
10	2	100	15.9 ± .6
19	2	100	15.3 ± 1.0
24.5	2-3	100	16.1 ± .4
			Average = 15.8 ± .2

deviations arise from having run a minimum of tests to conserve material, rather than from contradictions in results. The results are essentially consistent and thus we are assured that the requirement for testing at a sufficiently large diameter has been met for the 1,2-DP. Test diameters chosen for 2,2-DP and IBA were selected using the same criteria as for 1,2-DP, and it is assumed that the results are equally valid.

2. Detonation Initiation

To establish where detonation originates, initiation of 1,2-DP in the standard gap test geometry was attempted in 25.4 mm I. D. x 3.5 mm wall lead tubes 51 mm long with 14.0 mm of Plexiglas attenuation (the 50% point is 15.8 mm). However, using the streak camera to look down into the tube, no detonation light was observed. Similar shots with nitromethane using a slanted cover glass to eliminate the meniscus established a "50%" point of 3.8 to 5.1 mm of Plexiglas using light as a criterion for detonation. On the other hand, using witness plates or half-length CRISP wire we have found the 50% point to be 12.0 mm. Figure 2 shows a streak camera photograph of a shot in which 3.8 mm attenuation was used. In this shot the detonation is initiated at the wall of the

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FIG. 2 DETONATION INITIATION IN NITROMETHANE

tube. In these tests a 6 mil steel shim was used to seal the bottom. Replacing the steel shim by 2 mils of Magic Mending Tape,* the detonation light "50%" point is 6.4 to 9.4 mm of Plexiglas for nitromethane and the reaction is again wall-initiated. Table IV summarizes these results, which we are presently at a loss to explain.

*Trade Mark - 3M Company.

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Table IV

GAP SENSITIVITY OF NITROMETHANE IN I.D. LEAD TUBES

25.4 mm x 3.5 mm wall thickness

Method of Observing Detonation	6 mil Steel Shim (SS) or 2 mil Magic Mending Tape (MMT) Used to Seal Bottom	Sensitivity (mm of Plexiglas Attenuator)
Half-length CRISP	SS	11.8 ± 0.14
Witness Plate	SS	12.1 ± 0.14
Detonation Light	SS	3.8 - 5.1
Detonation Light	MMT	6.4 - 9.4

3. Attenuator Calibration

Figure 3 shows a new series of calibrations of the donor system used in the gap test using mirror cut-off measurements described previously.⁶ The open figures define calibrations using an explosive train consisting of a 1½ inch plane wave generator boosting a tetryl pellet (1-5/8" diameter x 1" thick), i.e., the type of explosive train used in all gap testing reported here. The closed circles define calibrations using two such tetryl pellets. Note that there is no grouping of the data on the basis of the two types of explosive train. A comparison of the gap sensitivities of several explosives for the same two donor systems is contained in Table V. Here it is seen that the two donor systems produce equivalent gap values. It is therefore concluded that the two systems are equivalent in the gap test.

Figure 4 shows a previous calibration of the card gap test used to obtain 50% point pressures of previous reports.⁷ The pressures for a

⁶ Technical Progress Report 64-4, Quarterly, June 15 - September 14, 1964, p. 3.

⁷ Technical Progress Report 64-4, Quarterly, June 15 to September 14, 1964, p. 10.

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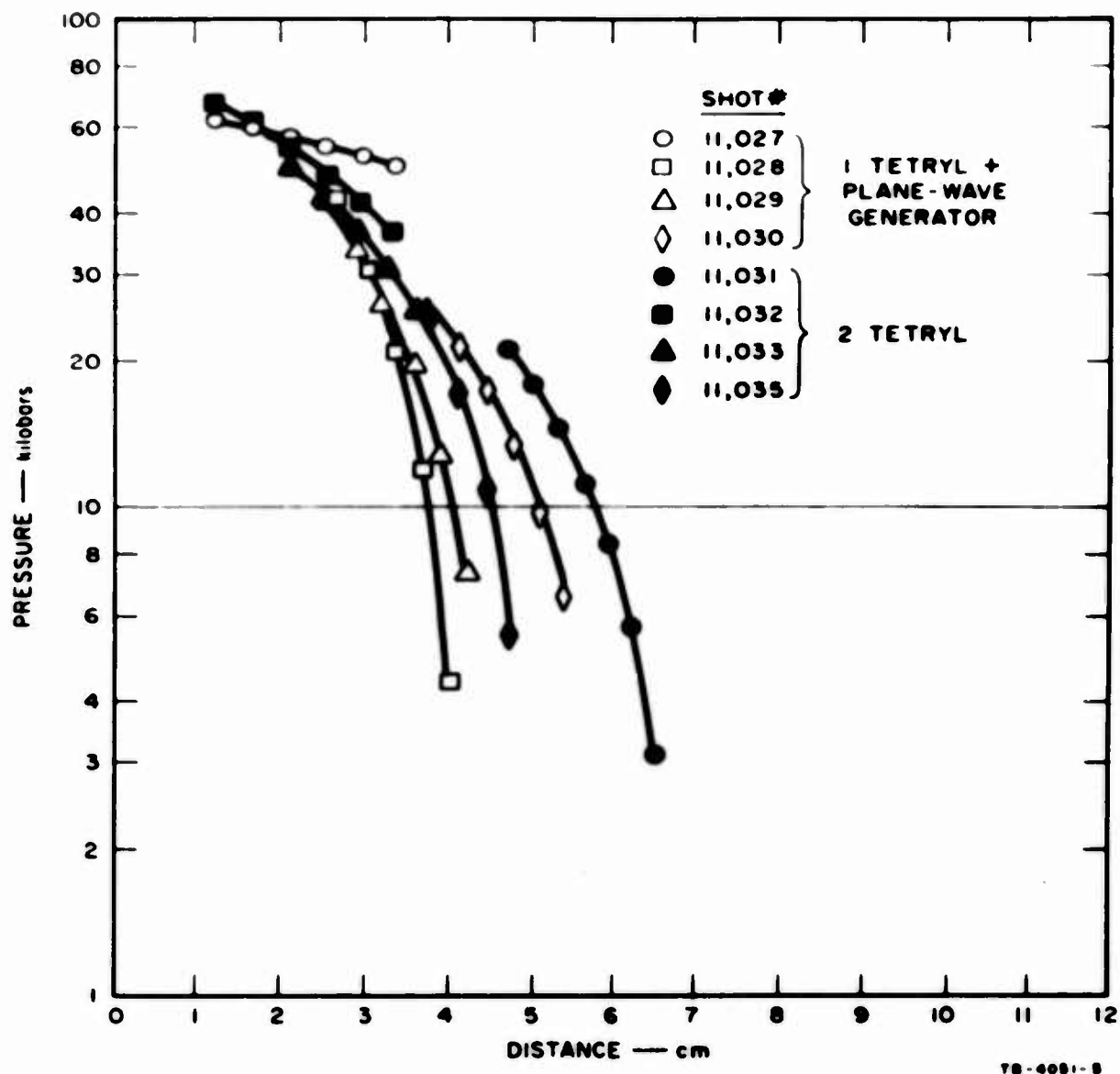


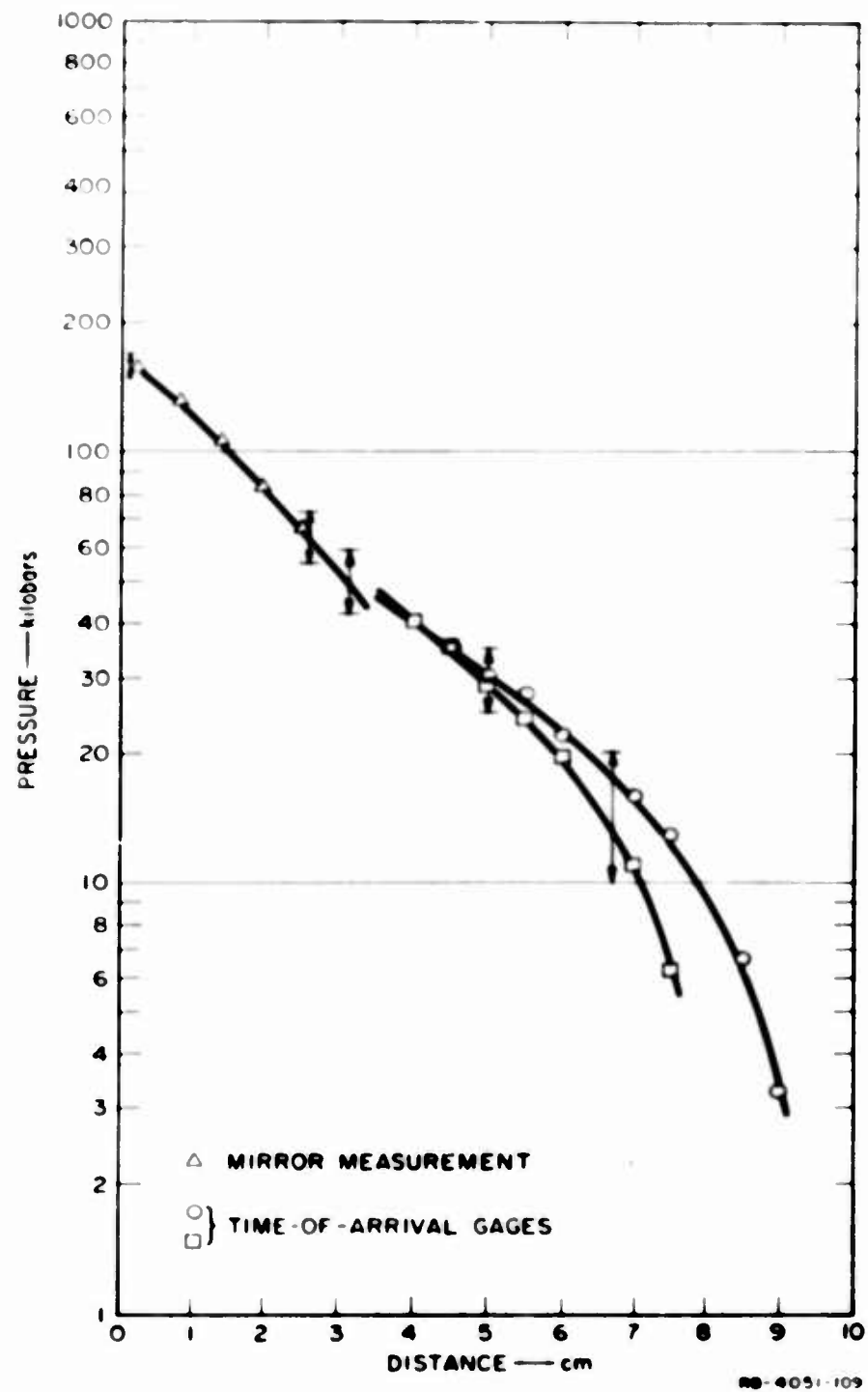
FIG. 3 CALIBRATION OF CARD GAP TEST

Table V
GAP SENSITIVITIES FOR TWO DONOR SYSTEMS

Compound	Sensitivity (mm of Plexiglas Attenuator)	
	Plane Wave Generator and 1 Tetryl Pellet	2 Tetryl Pellets
Comp B	34.4 ± 0.4	33.9 ± 0.6
RDX	41.5 ± 0.4	40.5 ± 0.6
Nitromethane	11.1 ± 0.8	11.4 ± 0.3
Tetryl	49.4 ± 0.4	52.1 ± 1.3

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**FIG. 4 CALIBRATION OF CARD GAP TEST —
PREVIOUS CALIBRATION**

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given gap thickness are higher than those in Fig. 3. This may have resulted from using a new batch of tetryl pellets to obtain the calibration of Fig. 3. In both calibrations the major source of scatter probably is the irreproducibility of the donor components.

D. Future Plans

Shots in steel hypodermic tubing of 1.2, 3.7, and 5.0 mm inside diameter are planned to establish the failure diameter of 1,2-DP and 2,2-DP in thin-walled confinement. We have found the failure diameter of IBA to be 10-15 mm in lead tubes but have established no lower limit for the 1,2- and 2,2-DP. By observing case expansion with a framing camera and using ionization probes at the ends of the tubes, we hope to measure detonation velocities which will be used to determine if detonation occurs.

Further observations of detonation light produced by nitromethane and the NF compounds in 25.4 mm I.D. lead cups using various attenuations are planned. Witness plates and the streak camera will be used on the same shot in order to see if the two detonation observation methods lead to different apparent sensitivities.

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III LOW VELOCITY REACTION WAVES

A. Introduction

The purpose of this work is to determine if the NF compounds are able to sustain a low velocity reaction regime which would be as destructive as a high velocity detonation. Experiments have been run on nitromethane and a 90% (by weight) nitromethane (NM) - 10% tetranitromethane (TNM) mixture in order to develop methods of observation.

B. Background

It has been established that conventional gap tests with a witness plate and even more sophisticated gap tests using continuous wire techniques detect only high velocity detonation waves. It has also been established that with certain liquids, explosions whose linear propagation rate is in the vicinity of 2 mm/ μ sec can be reliably initiated. These low velocity waves, which are not detected by gap tests, are of the same order of violence as the high velocity ones and can be initiated with relatively weak shocks--certainly much weaker than those required to initiate conventional high velocity detonations.

Van Dolah and co-workers at the Bureau of Mines have reported⁴ their work with mixtures of nitroglycerine (NG) and ethylene glycol dinitrate (EGDN), and of nitromethane (NM) and tetranitromethane (TNM). Their experiments consist mainly in subjecting samples of these liquids to relatively weak shocks, thereby initiating low velocity waves which they report to be stable. They have measured pressures in these waves and report them to be of the order of 5 kbars. Also, in a series of back-lighted schlieren photographs they have been able to examine the precursor waves to reaction in the NG-EGDN mixture. Their results using different types of confinement led them to postulate a mechanism.

Starting with the liquid confined in a steel tube and subjected at one end to weak shock, Fig. 5 is their pictorial representation of the steady state for the set of coordinates in which the camera observer moves at the detonation velocity.

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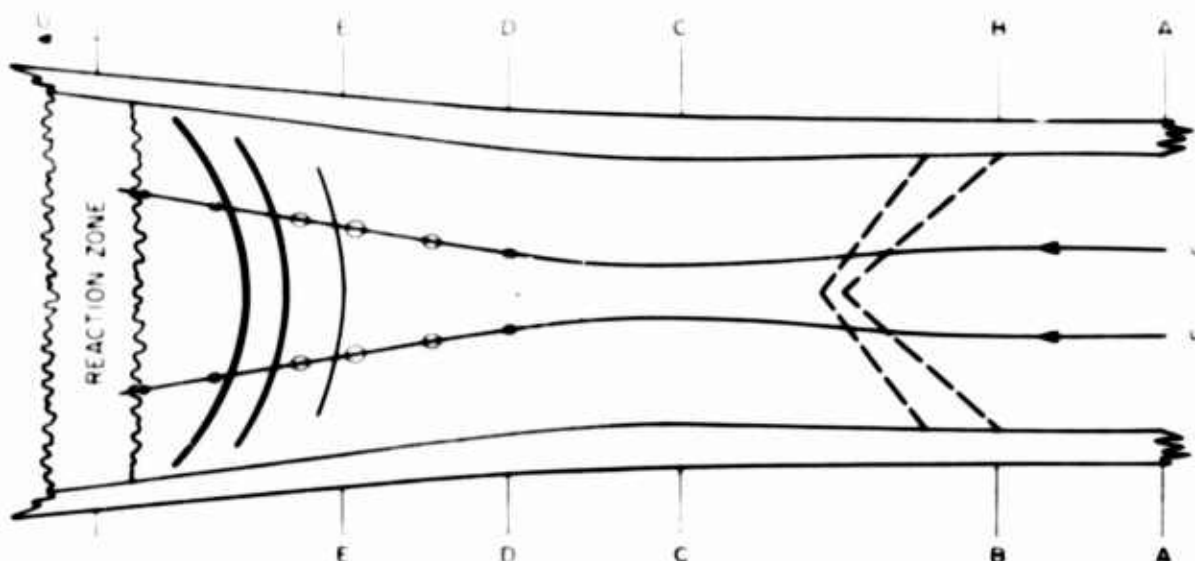


FIG. 5 PICTORIAL REPRESENTATION OF A STEADY STATE LOW-ORDER DETONATION IN A CONFINED LIQUID EXPLOSIVE

- (1) The undisturbed liquid in Section "AA" moving along the particle paths "uu" is first compressed by the shock waves delivered to the fluid by the precursor wall shocks located at "BB."
- (2) The compressed fluid then moves into an expanded region, beginning at "CC," where the wall begins to move outward due to the pressures generated in the reaction zone.
- (3) The liquid continues to expand and eventually cavitates in the region of "DD."
- (4) The cavities grow until they encounter the pressure field in the liquid near the reaction zone. This point is labeled "E" in the figure.
- (5) On entering the pressure field at "EE," the cavities collapse generating the high pressures and temperatures necessary to cause sustained chemical reaction.

The reaction zone can then be visualized as the combined effect of a multitude of microscopic reaction centers. The important feature of this model is the hypothesis that a low pressure region exists behind the precursor wall shock and ahead of the pressure field due to the reaction zone. This may occur if the initial expansion of the container wall takes

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place at a point appreciably ahead of the reaction zone which, in turn, can occur if the velocity of such waves in the wall material is greater than the velocity of weak shocks (near sonic velocity) in the liquid. This model offers an explanation of Van Dolah's observation that low velocity reactions in lead tubes and in tubes with thin walls are unstable.

In contrast to these experiments with weak shocks we have Seely's experiments³ with the difluoroamino compounds using very strong shocks. He reports the initiation of low velocity waves in diameters below the normal failure diameter but suggests no mechanism for the process.

Thus the current literature offers such considerable evidence that the occurrence of low velocity detonations can no longer be seriously questioned. What remains is to establish the mechanism so that predictions of behavior can be made in situations of interest.

C. Experimental Procedures and Results

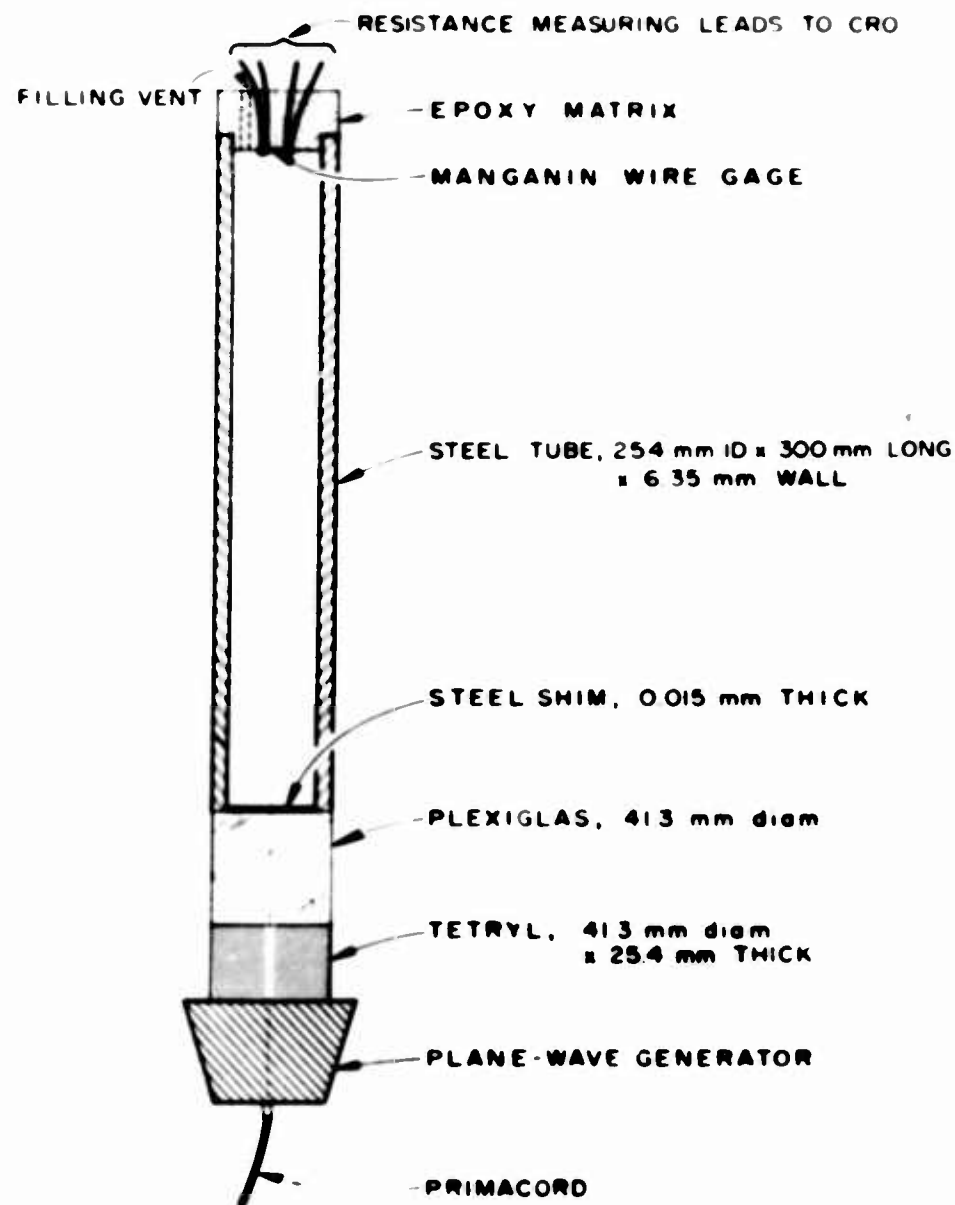
In the development of suitable experimental techniques our first measurements were made with a 10% (by weight) TNM-90% NM mixture. Measurements were made in (a) instrumented steel tubes, and (b) windowed cells with rectangular cross sections in which the processes were photographed.

The arrangement utilizing the instrumented steel tubes is illustrated in Fig. 6. The donor system consists of a Composition C-2 plane wave generator followed by a 1-5/8-inch-diameter x 1-inch-thick tetryl pellet. The attenuator is a 1-5/8 inch-diameter Plexiglas pellet. We estimate that this produces approximately a 30-kbar shock wave in the liquid acceptor. The pressure gauge⁴ is of fine manganin wire mounted carefully so as to be exactly at the surface of an epoxy disc. The impedance of the epoxy is essentially the same as that of the liquid and, because of the fineness of the wire, the liquid attains the pressure of its environment within a period much shorter than a microsecond. From the change in resistance of the wire one can calculate the pressure of an imposed shock wave.

⁴D. D. Keough, D. Bernstein, and R. F. Williams, "Piezoresistive Pressure Transducer," ASME Publication 64-WA/PT-5.

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TM 4051-3

FIG. 6 TEST ARRANGEMENT FOR STUDIES IN STEEL TUBES

Subsequent to initiation of the explosion, an oscilloscope is triggered by a switch at the tetryl-Plexiglas interface. The data recorded give the pressure of the wave reaching the gauge and the transit time of the wave from the switch to the gauge surface. The transit time through the Plexiglas and the sample length are known. Consequently, the average velocity of the wave to which the gauge responds can be calculated. The results are listed in Table VI and confirm the occurrence of these phenomena.

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Table VI

LOW VELOCITY PROPAGATION
10% TNM-90% NM IN STEEL TUBES

Record No.	Attenuator Thickness mm	Average Velocity in liquid mm/ μ sec	Recorded Shock Pressure kbars	Pulse Duration
123	25.4	1.9		~15 μ sec
132	50.8	1.7	16	
14163-2	50.8	1.8	14	
14164-2	50.8	1.1	10	
14164-3	50.8	1.1	5*	

*Unreliable value due to instrumental difficulty.

In addition to making the pressure measurements, we have tried to measure velocities with the continuous wire. Apparently the shock temperature and, therefore, the extent of ionization were very low, for no data were recorded. Also, from Record No. 14163-2 (the gauge used in this test functioned properly for 45 μ sec), we were able to establish that, in at least this one case, the pressure was maintained for about 15 μ sec.

The tests with the windowed cells utilized the apparatus shown in Figs. 7 and 8. The same shock donor was used as in the previous tests with the steel tubes. The optical system provided a shadowgraphic record of the refractive index changes within the liquid during the transit of the shock and the reaction wave.

The results of a typical test are further evidence that low velocity processes occur. Figure 9 includes four frames selected from the sequence of twenty-five obtained during one experiment. The first picture shows the undisturbed charge. (What appear to be a bubble on the bottom and irregularities of the wall surface were, in fact, small amounts of the

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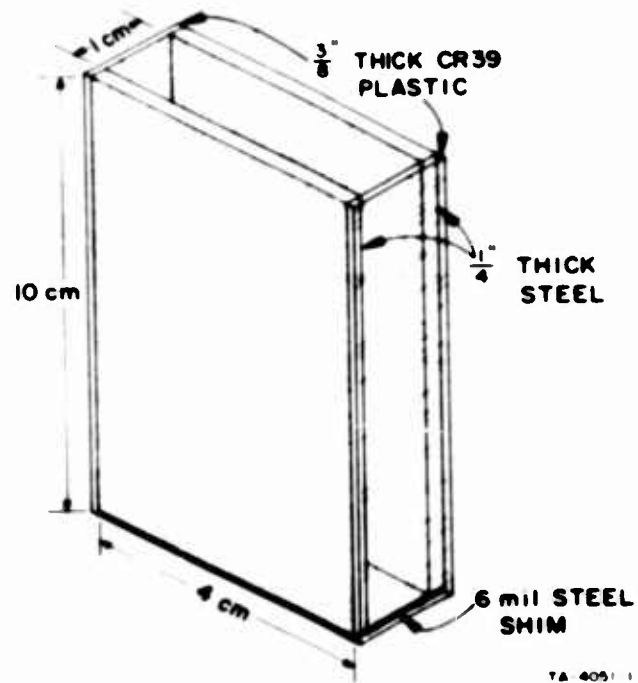


FIG. 7 TEST ARRANGEMENT FOR OPTICAL STUDIES

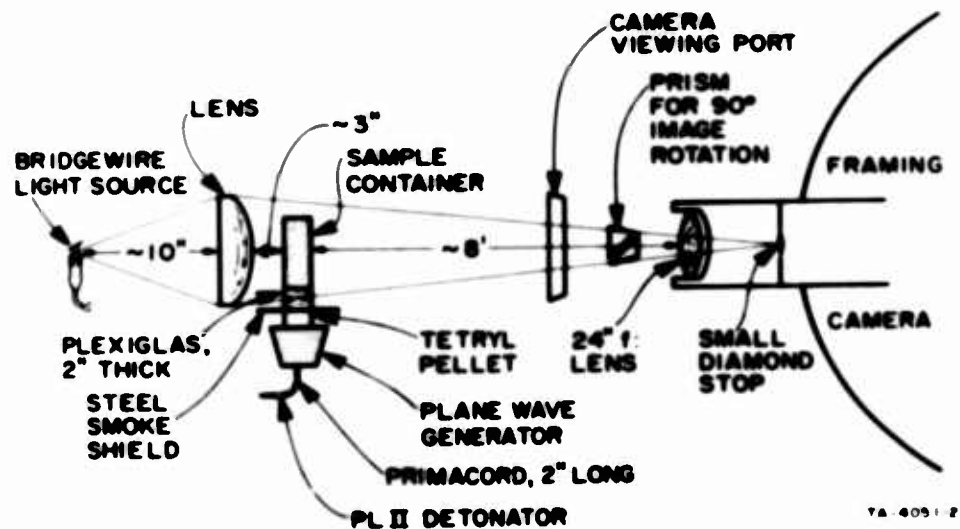
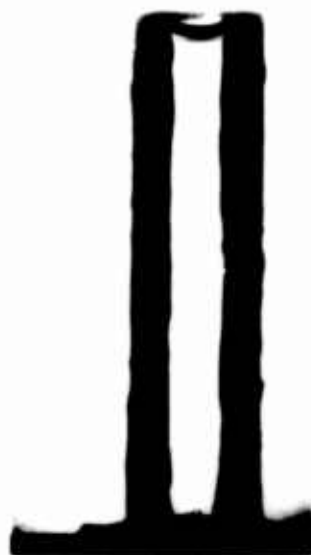


FIG. 8 SHADOWGRAPH TECHNIQUE FOR LOW VELOCITY WAVE STUDIES

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START — 0 μ seconds



~6 μ seconds SHOWING PRECURSOR
SHOCK WAVE AND STRUCTURED
REACTION ZONE



~ 10 μ seconds SHOWING PRECURSOR
SHOCK WAVE, MULTIPLE REFLECTIONS,
AND REACTION ZONE.



~ 16 μ seconds SHOWING HIGHLY
STRUCTURED PRECURSOR WAVE
AND STRUCTURED REACTION ZONE

18-4051-4

FIG. 9 PHOTOGRAPHS OF LOW VELOCITY
PROPAGATION IN STEEL

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cement used to attach the plastic to the steel. They had no effect upon the propagation.) The second frame--taken 6 μ sec later--clearly shows the precursor waves as well as a structured reaction zone. The third frame--10 μ sec after the first--shows the more highly developed precursor region followed by the reaction zone. The fourth frame--16 μ sec after the first--shows a continuation of these phenomena plus a number of bubbles. Actually, the first bubbles become visible about 12 to 14 μ sec after the stage shown in the first picture. In none of these pictures have we been able to detect expansion of the metal wall.

Thus the photograph shows a wave which has the characteristics of Van Dolah's bow wave proceeding through the liquid, with a velocity ~ 5.9 mm/ μ sec, approximately the sonic speed of the steel. Moreover, we see a rather highly structured reaction zone which forms well behind this bow wave and has a much lower velocity, ~ 1.7 mm/ μ sec. It is apparently this second regime to which the pressure gauge responds in the other shots. We have not yet detected evidence of bubble formation or of expansion of the tube prior to reaction. We cannot emphasize too strongly that these conclusions are interpretations of only the very beginning of an extensive program, but it seems likely that there may be some significant difference between our results and those reported by the Bureau of Mines.

To find out if confinement materials of various physical properties and thicknesses have any effect on LVD, various materials were used for the side walls of the windowed sample containers (Fig. 7). These side walls were constructed of 1/4 inch and 1/16 inch thick sections of lead, steel, aluminum, and CR-39. One-sixteenth inch thick CR-39 windows were used in all cases. The wave structure is as shown in Fig. 9 for Al, steel, and CR-39. For lead the structure is as shown in Fig. 10 in which there is no precursor shock feeding into the liquid from the walls. The results are presented graphically in Fig. 11-16, where the velocity of the leading edge of the low velocity wave or structured reaction zone (see Fig. 9) is plotted against distance into the charge. Since average velocity is calculated from the distance traveled between frames in the

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framing camera sequence, this velocity has been arbitrarily assigned to the mid-point of the wave positions in adjacent frames. The observed fluctuations of about $\pm 0.4 \text{ mm}/\mu\text{sec}$ are in large part due to subjective reading error caused by diffuseness of the wave front.

The following conclusions may be drawn from these graphs: (1) There is no apparent difference in behavior of the waves in $1/4$ inch versus $1/16$ inch confinement in aluminum, steel, lead, or CR-39 for the mixture or pure nitromethane. (2) With $1/4$ inch steel and aluminum and with 1 inch of Plexiglas attenuation the low velocity wave attenuates until it is 6 cm from the donor, beyond which the velocity is the same as that attained with 2 inch of Plexiglas attenuation. This velocity is $1.6 \pm 0.4 \text{ mm}/\mu\text{sec}$. (3) With $1/4$ inch lead and 1 inch of Plexiglas attenuation



FIG. 10 PHOTOGRAPH OF LOW VELOCITY
PROPAGATION IN LEADS

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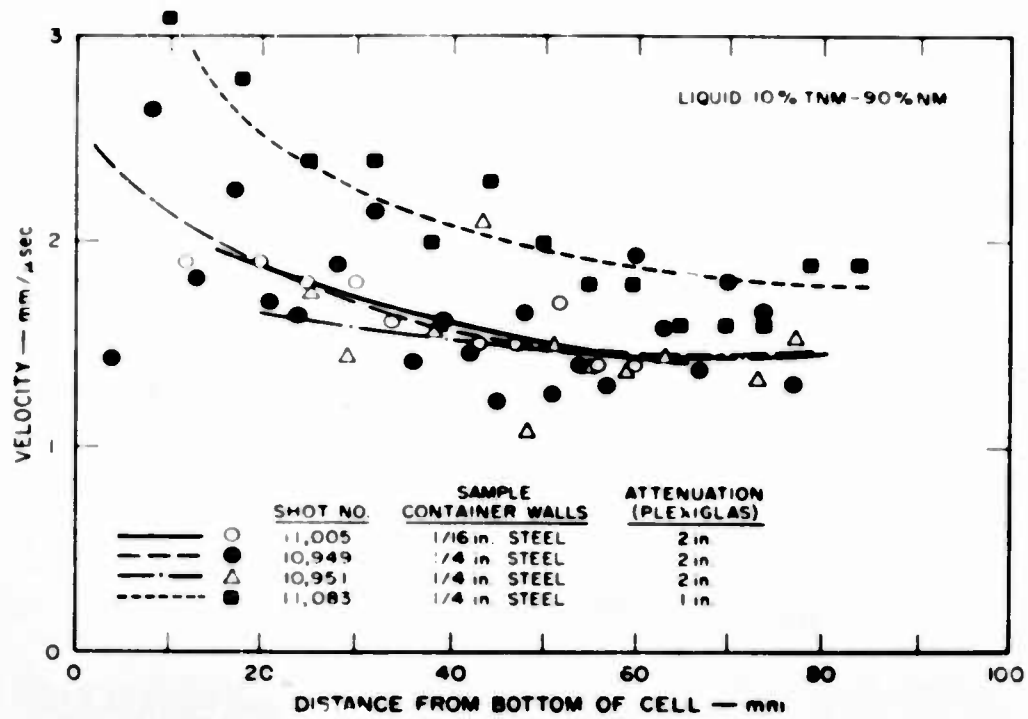


FIG. 11 GRAPH OF LOW VELOCITY PROPAGATION IN 10% TNM — 90% NM IN STEEL

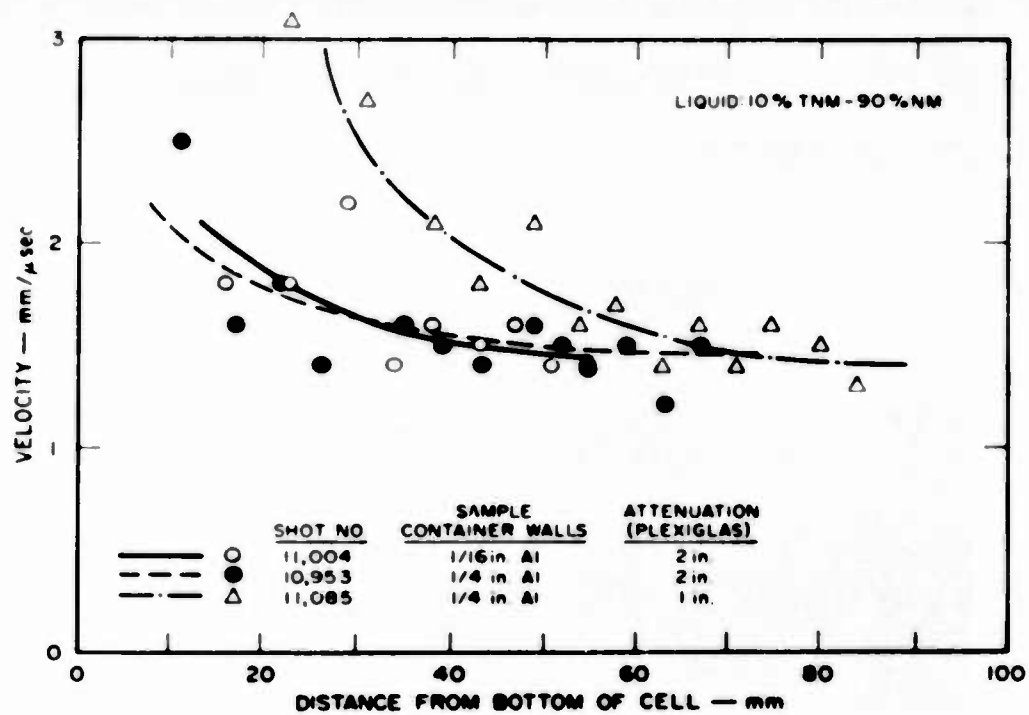


FIG. 12 GRAPH OF LOW VELOCITY PROPAGATION IN 10% TNM — 90% NM CONFINED IN ALUMINUM

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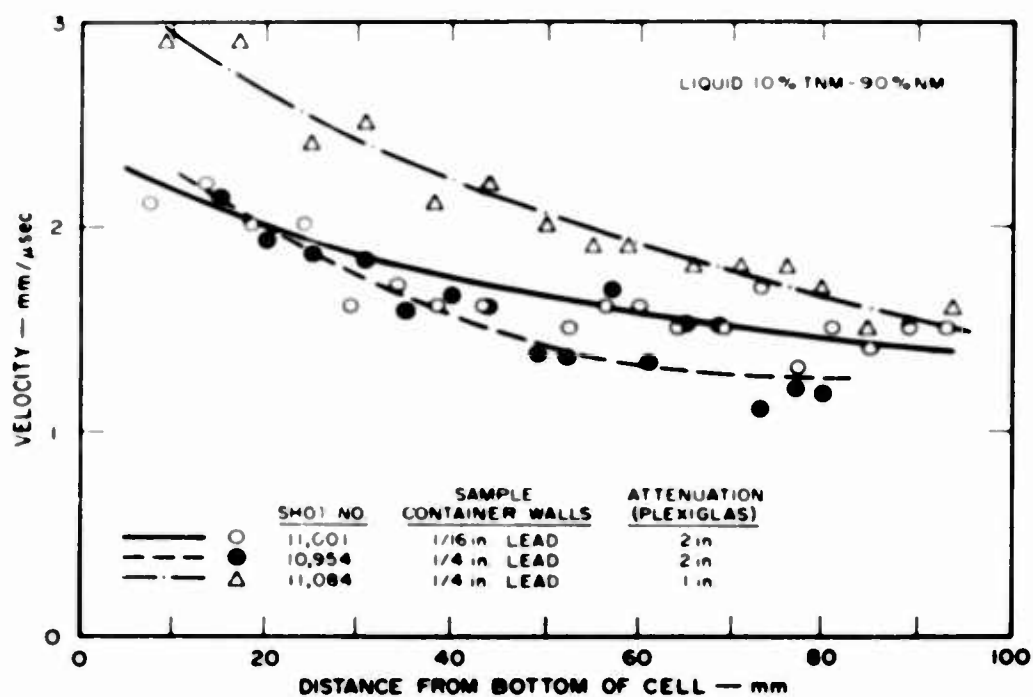


FIG. 13 GRAPH OF LOW VELOCITY PROPAGATION IN 10% TNM — 90% NM CONFINED IN LEAD

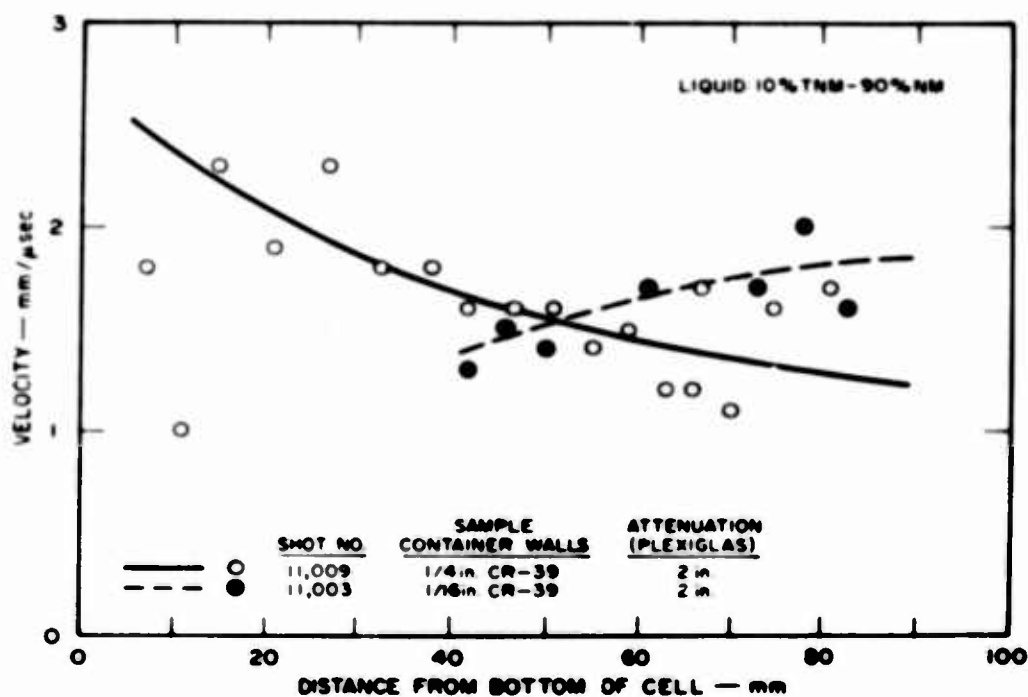


FIG. 14 GRAPH OF LOW VELOCITY PROPAGATION IN 10% TNM — 90% NM CONFINED IN CR-39

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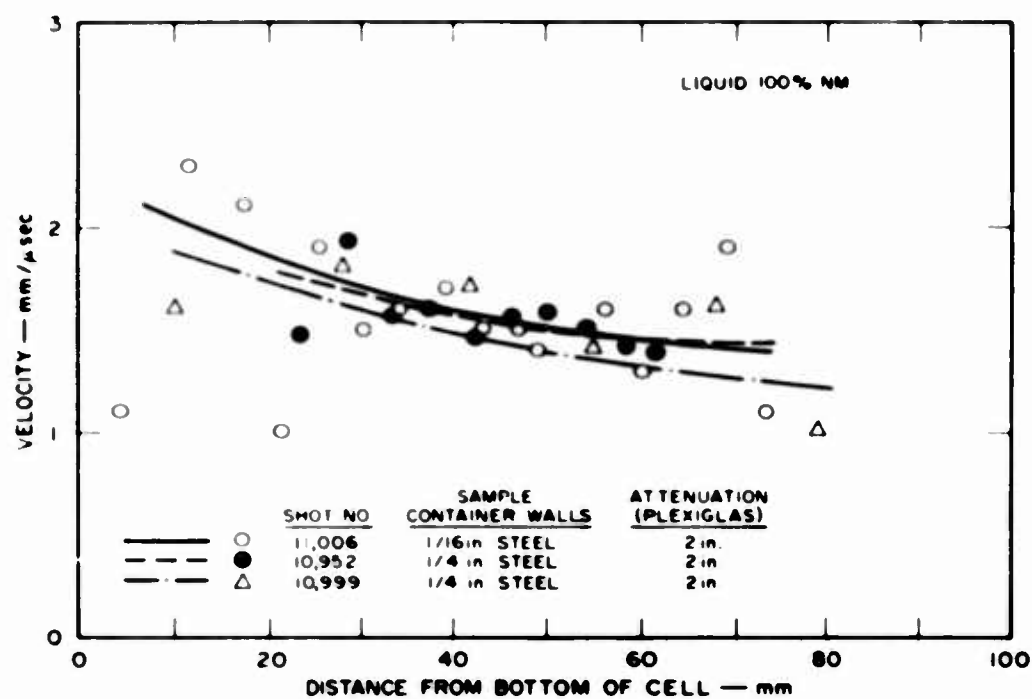


FIG. 15 GRAPH OF LOW VELOCITY PROPAGATION IN 100% NM CONFINED IN STEEL

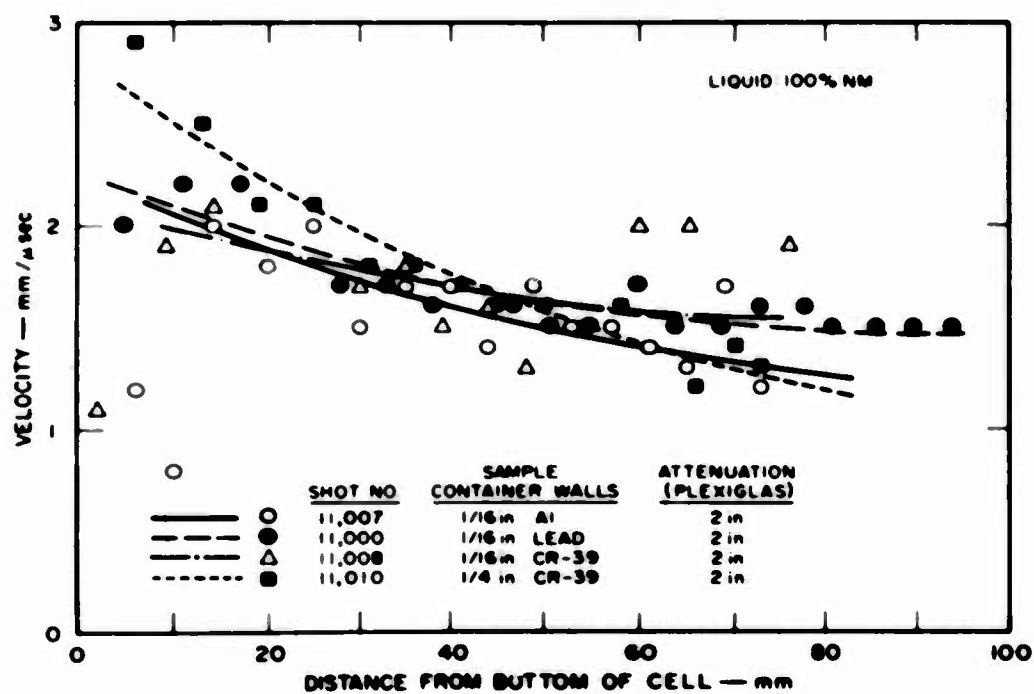


FIG. 16 GRAPH OF LOW VELOCITY PROPAGATION IN 100% NM CONFINED IN VARIOUS MATERIALS

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the low velocity wave has not attenuated sufficiently in 10 cm of travel to reduce its velocity to that attained with 2 inch of attenuation. (4) the "stable" velocities in all confinements are 1.5 ± 0.4 mm/ μ sec in both the mixture and pure nitromethane. Figure 17 is the graph of the data from the photographs of water with 1 inch of Plexiglas attenuation in a steel sample container when shocked under these conditions. Although the graph clearly shows a decaying trend in the velocity not seen in the mixture or nitromethane, the decay is just reaching 1.6 mm/ μ sec near the end of the sample container. Therefore, longer charges are necessary to detect clearly the difference between a low velocity wave and the shock waves produced in an inert liquid.

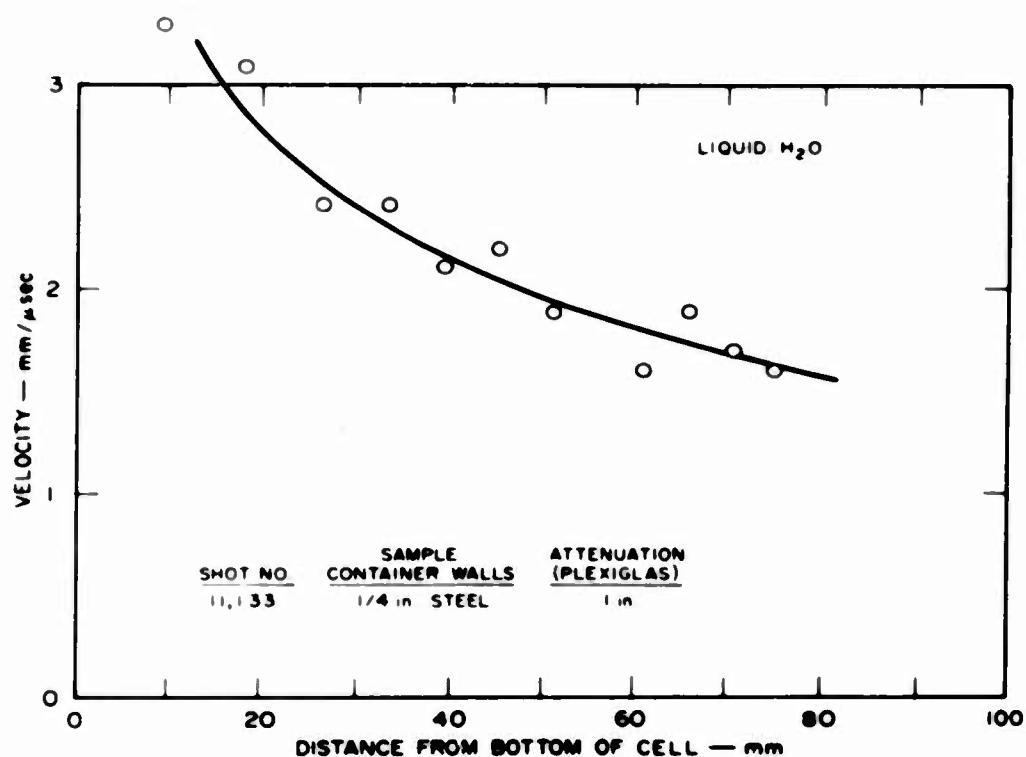


FIG. 17 GRAPH OF LOW VELOCITY PROPAGATION IN H₂O CONFINED IN STEEL

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D. Future Plans

More experiments will be conducted with pure nitromethane, the TNM/NM mixture, and water. Sample containers of lead and aluminum three times longer than used previously (30 cm) will be employed to try to differentiate between LVD and non-reactive shock propagation in liquids by measurement of wave velocity. These experiments should also tell something about the stability of LVD in long charges. If these plans are successful the NF_3 compounds will be examined similarly to observe their behavior.

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IV ADAPTATION OF THE JANAF BOOSTER TEST

(A.B. Amster, J.A. Neff, D.B. Moore, J. Berke, and R.W. McLeod)

A. Introduction

High energy liquids are often exposed to conditions, such as extremes of high temperatures and pressures, which may change their susceptibility to shock initiation. Moreover, many high energy materials are condensed only under such extreme conditions. There exists a need for a detonation sensitivity test applicable to those situations. This report outlines studies made to adapt the current JANAF test⁹ for use under the following conditions:

$$77^{\circ}\text{K} < T < 373^{\circ}\text{K}$$

$$1 \text{ atm.} < P < 10 \text{ atm.}$$

Two methods were used which rely upon measuring detonation velocity, rather than the present method of utilizing damage to a witness plate, to determine whether detonation occurred. The first method, perhaps the simpler, was an adaptation of the method of Dautriche.¹⁰ This method, shown schematically in Fig. 18 compares the detonation velocity of a known material with that of the sample under study.

The tetryl initiates the detonating fuse, which in turn indicates the explosive sheet at the "start" position. This detonation propagates further along each "finger" of the explosive sheet.

A strong wave in the sample will also initiate the remaining pieces of fuse in order. Where the detonation waves collide within the fingers, dents are created in the witness plate deeper than those left by a unidirectional wave. The result of a typical shot is shown in Fig. 19. From the position of the dents and the properties of the system, the wave velocity within the sample can be calculated (see Appendix A). This method has the advantage that no elaborate electrical equipment is necessary.

⁹ "Liquid Propellant Test Methods, Test No. 1," LPIA (March, 1960).

¹⁰ H. Dautriche, "The Velocity of Detonation in Explosives," Compt. rend., Vol. 143, 641-44 (1906) Chem. Abstr. 1, 357-8 (1907).

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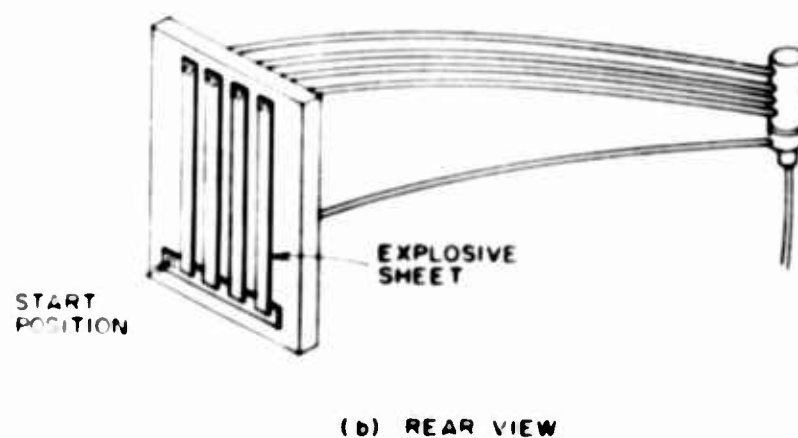
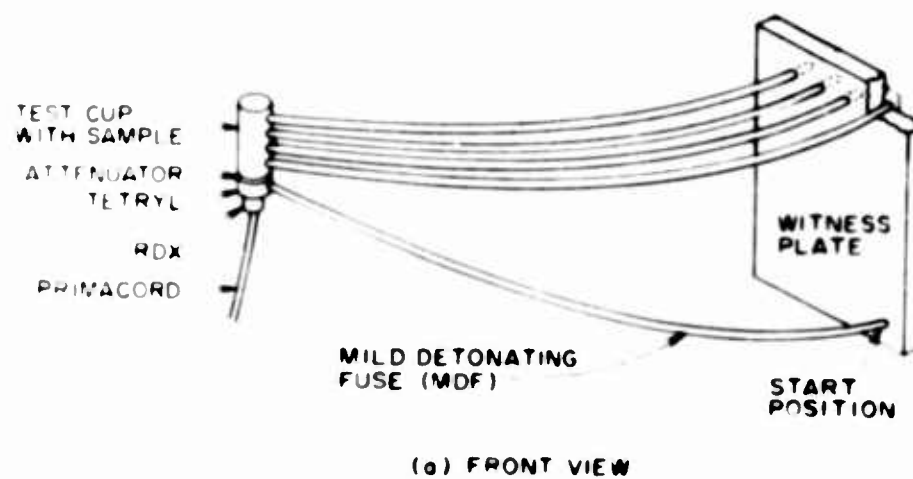


FIG. 18 TEST ARRANGEMENT

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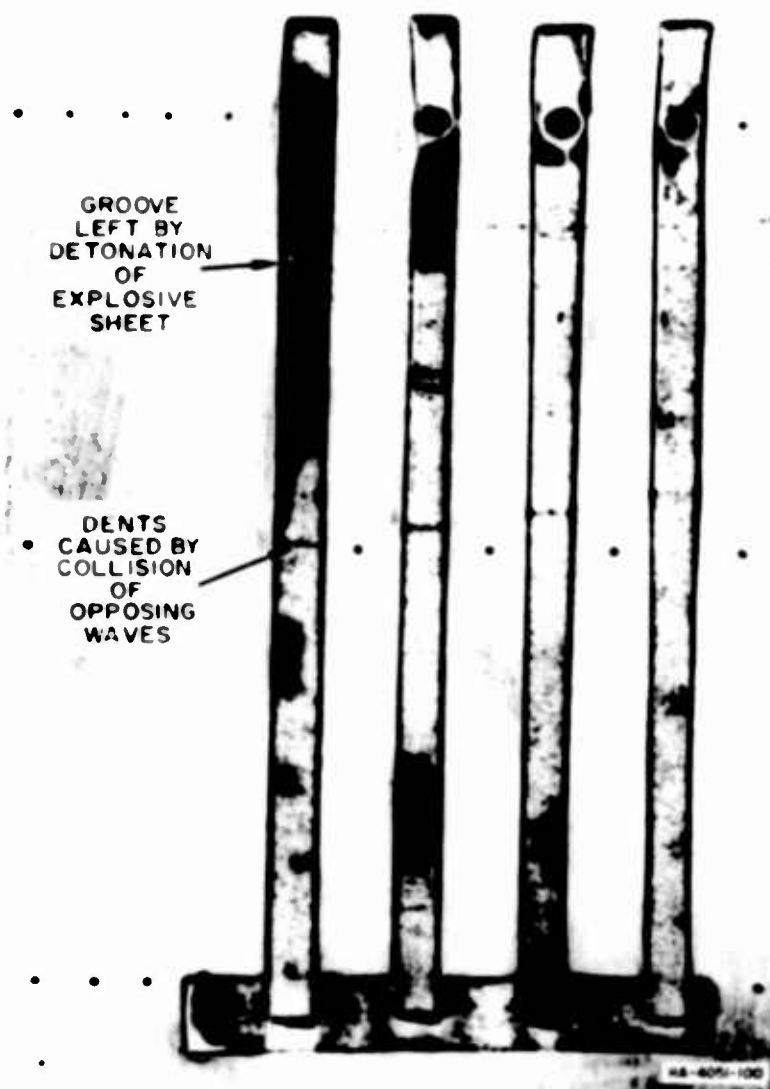


FIG. 19 TYPICAL TEST RESULT — WITNESS PLATE

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A second method utilizes a resistance wire³ in the detonation cup and a constant current power supply to yield a continuous detonation velocity record on an oscilloscope. This method is considerably more precise and, therefore, less ambiguous. It has the disadvantage of requiring a modest amount of electronic equipment and some considerable operator skill.

Both the explosive probe method and resistance wire method operate successfully. They are described further in the following sections.

The procedures for manipulating the test compounds will vary with their properties (e.g., toxicity, vapor pressure, etc.). We describe, in the following text, procedures employed with N_2F_4 at low temperature. We believe the materials and the methods are sufficiently representative to establish the general value of this extended test.

B. Experimental

1. Modified Dautriche Method

a. Test Development at Ambient Conditions

For each shot a standard test cup³ is modified as shown in Fig. 20a and an aluminum witness plate is prepared as in Fig. 20b.

Five pieces of MDF*, 20.00 inch long are cut by a razor blade on a piece of wood or Micarta. Five 1/2 inch wide strips of sheet explosive are also cut. One is about 4 inches long, the other four are 8.00 inches. Using precision scales and squares, the short strip is cemented parallel to the short edge of the plate with one end over the single hole. The long strips are cemented parallel to each other, one end over each of the remaining holes and the other end over, and in contact with, the short strip (see Figs. 20c and 21a).

*Trade Mark--E. I. duPont de Nemours and Co. (Mild Detonating Fuse).

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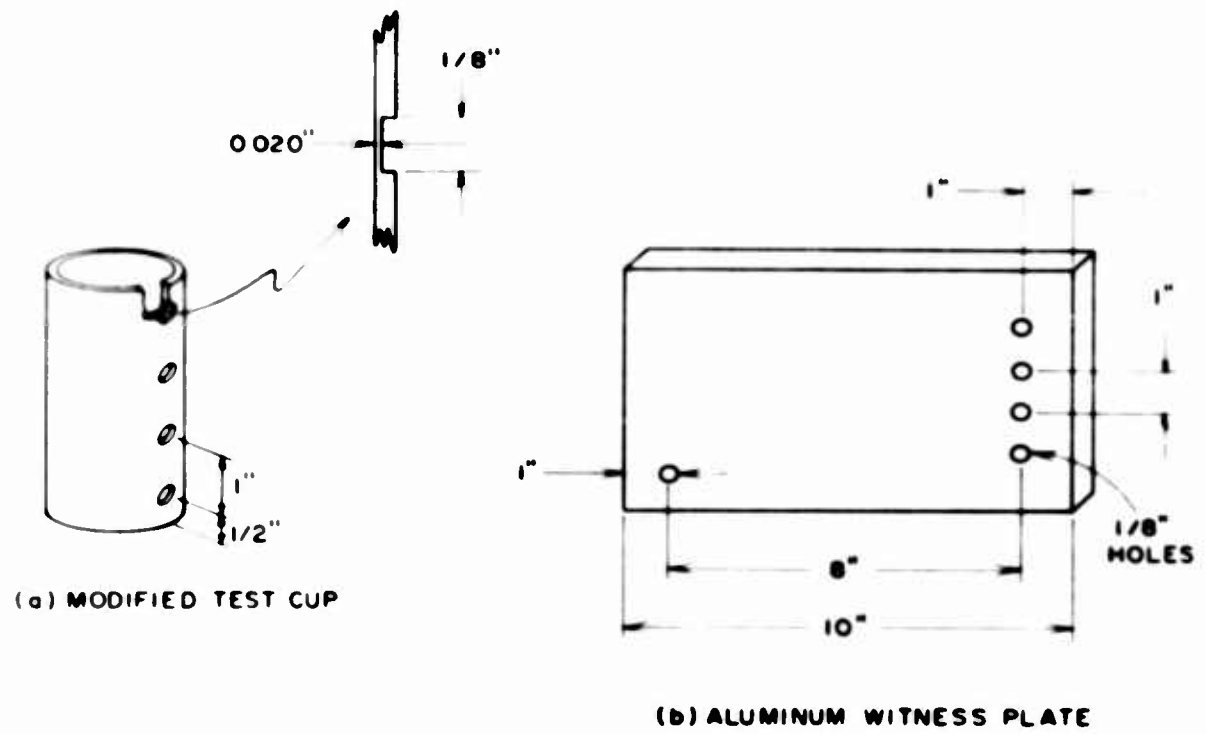


FIG. 20 TEST COMPONENTS

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(a) MDF, PLATE, AND SHEET EXPLOSIVE



(b) MDF AND WITNESS PLATE



(c) TEST CUP, BOOSTER AND MDF

FIG. 21 ASSEMBLED COMPONENTS

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The test cup and booster are assembled in prescribed fashion and the witness plate secured nearby. One end of each of the 20-inch lengths of MDF is inserted through a hole in the plate until it contacts the explosive sheet (Fig. 21b). The other ends are put in place on the charge (no auxiliary booster is used) as shown in Fig. 21c, four along the cup wall, one to the initiator. All ends are cemented securely in place.

The results of a series of tests to evaluate the method are presented in Table VII. Shots 1, 4, and 5 established a useful witness plate thickness: viz. 1/2 inch aluminum. Shots 2, 3, and 6 conducted with liquid nitromethane demonstrated that detonation of a liquid in the test cup would propagate through the walls to initiate the MDF and that the plate dents could be used to calculate velocity.

A number of control experiments were conducted. Using sheet explosive to line the cup (Tests 4 and 5) or unconfined Comp. B, (Test 11) it was again demonstrated that a stable high velocity could be detected reliably.

Tests 12 through 16 established that most reliable results were obtained using 20 grain per foot PETN, filled MDF, and Deta Sheet D-1 sheet explosive.

A failing (i.e., nonpropagating) detonation wave, should be detected by a decelerating wave velocity rather than by failure of the MDF to detonate. Shots 7 and 8, conducted on either side of the sensitivity limit of nitromethane demonstrated that the explosive witness met this requirement. Thus, with 40 cards nitromethane detonates, as confirmed by the approximately constant high velocity calculated at each station. However, with 60 cards nitromethane does not propagate detonation as evidenced by the decreasing velocity recorded. This result can be compared with the results of Shot 10 using water: the low velocity initially recorded decays rapidly so that no record is obtained at the third and fourth fingers. These measurements confirm that the test is a high velocity sensor rather than a detonation sensor, the desired result.

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Table VII
RESULTS OF EXPLOSIVE WITNESS SENSITIVITY TEST EVALUATION

Shot No.	Sample	Booster	Attenuator	Detonating Fuse	Explosive Sheet	Witness Plate	Shock Velocity (mm/μsec)			Remarks
							1	2	3	
1	None	None	None	MDF	0.050" Data Sheet ^o D	1/4" Aluminum				Plate severed
2	Nitromethane 20°C	Tetryl (2 pellets)	None	20 grain PETN	506-D ^o	1/4" Aluminum	3.8	3.8	5.3	
3	Nitromethane 20°C	Tetryl (2 pellets)	None	20 grain PETN	506-D ^o	1/4" Aluminum	4.9	5.4	5.6	
4	506-D lining cup	Tetryl (1 pellet)	None	20 grain PETN	506-D ^o	1/4" Aluminum	7.3			Plate severed at points of convergence
5	506-D lining cup	Tetryl (1 pellet)	None	20 grain PETN	506-D ^o	1/2" Aluminum			6.1	#2 probe severed by fragment
6	Nitromethane 20°C	Tetryl (1 pellet)	None	20 grain PETN	506-D ^o	1/2" Aluminum	5.8	6.0	6.1	
7	Nitromethane 20°C	Tetryl (2 pellets)	40 cards	20 grain PETN	506-D ^o	1/2" Aluminum	4.9	7.1	6.3	
8	Nitromethane 20°C	Tetryl (2 pellets)	60 cards	20 grain PETN	506-D ^o	1/2" Aluminum	2.9	2.6		4th intercept off plate
9	Nitromethane 20°C	Tetryl (2 pellets)	50 cards	20 grain PETN	506-D ^o	1/2" Aluminum				No record obtained (Human error)
10	H ₂ O 20°C	Tetryl (1 pellet)	50 cards	20 grain PETN	506-D ^o	1/2" Aluminum	2.63			3rd and 4th intercepts off plate
11	Nitromethane 20°C	Tetryl (1 pellet)	None	20 grain PETN	506-D ^o	1/2" Aluminum	6.9	7.9	7.1	Ideal velocity = 7.8 mm/μsec
12a	Nitromethane 20°C	Tetryl (2 pellets)	40 cards	20 grain PETN	50 -D ^o	1/2" Aluminum	3.01	-	-	MDF functioned properly
12b	Nitromethane 20°C	Tetryl (2 pellets)	40 cards	20 grain RDX	506-D ^o	1/2" Aluminum	-	-	-	MDF did not initiate
13	Nitromethane 20°C	Tetryl (2 pellets)	40 cards	20 grain RDX	0.045" Data Sheet ^o C-1	1/2" Aluminum				MDF did not initiate reliably
14	None	Tetryl (1 pellet)	None	10 and 20 grain PETN	0.045" Data Sheet ^o D-1 (green)	1/2" Aluminum	-	-	-	MDF did not initiate reliably (attempted simultaneous initiation of each length of MDF)
15	None	Tetryl (1 pellet)	None	10 and 20 grain PETN	0.045" Data Sheet ^o D-1 (red)	1/2" Aluminum				Initiated reliably
16	EL-506-D	Tetryl (1 pellet)	None	20 grain PETN	0.045" Data Sheet ^o D-1 (red)	1/2" Aluminum	Attempted simultaneous initiation			Reliable initiation accomplished
17	None	Tetryl (1 pellet)	None	20 grain RDX in liquid N ₂ and at 20°C	0.045" Data Sheet ^o D-1	1/2" Aluminum				Results reproducible but temperature dependent
18	None	Tetryl (1 pellet)	None	20 grain PETN in liquid N ₂ and at 20°C	0.045" Data Sheet ^o D-1	1/2" Aluminum				Results reproducible but temperature dependent
19	None	Tetryl (1 pellet)	None	20 grain PETN in liquid N ₂ and at 20°C	0.045" Data Sheet ^o D-1	1/2" Aluminum				Results reproducible but cold leg did not initiate
20	Nitromethane in liquid N ₂	Tetryl (2 pellets)	None	20 grain PETN	0.045" Data Sheet ^o D-1	1/2" Aluminum	5.5	6.2	4.5	All points obtained--good record
21	Empty cup	Tetryl (2 pellets)	None	20 grain PETN	0.045" Data Sheet ^o D-1	1/2" Aluminum				No. 1 intersection obtained. All others off plate

^oTrade Mark E. I. duPont de Nemours and Company.

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Experiments establishing the precision of the Dautriche method were made with tests using Comp. B and nitromethane at ambient temperature. Results (Table VIII) may be compared with reported values of 6.25 mm/ μ sec for nitromethane¹¹ and 7.93 mm/ μ sec for Comp. B.¹²

All of the measurements on Comp. B lie within 5% of both the reported value and the average of our measurements. The comparable figure for nitromethane is 10% for all but one of the measurements; for the exception the difference is 15%. Thus, under ambient conditions this method may be considered accurate to within $\pm 10\%$.

Table VIII

EXPLOSIVE WITNESS DETONATION VELOCITY MEASUREMENTS

Shot No.	Explosive	Velocity (mm/μsec)					Average
		Explosive Witness Stations					
		1-2	2-3	3-4	4-5	5-6	
11	Composition B	6.9	7.9	7.1			7.3
43		6.0	8.4	9.6	6.0	7.4	7.5
44		8.4	6.0	8.8	7.7	8.6	7.9
50		7.4	7.0	7.4	10.7	7.8	8.1
							Mean = 7.7
25	Nitromethane	5.5	5.3	5.7			5.5
30		6.1	6.1	5.7	5.4		5.8
33		6.6	5.3	4.0	12.3	5.3	6.7
34		4.1	9.5	6.6	4.3	8.0	6.5
40L		7.3	5.7	5.7	6.7	7.3	6.5
40R		7.6	5.1	6.1	6.7	7.3	6.6
							Mean = 6.3

¹¹ A. W. Campbell, W. C. Davis, and J. R. Travis, Phys. Fluids 4, 498 (1961).

¹² M. E. Malin, A. W. Campbell, and C. W. Mautz, J. Appl. Phys. 28, 63 (1957).

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b. Low Temperature Test Development

Low temperature behavior was examined and the results are shown in Tables VII (Shots 17-20), IX, and X. The performances of PETN- and RDX-containing MDF were found to be satisfactory in liquid nitrogen (77°K) and a reasonable velocity record was obtained using nitromethane at the same temperature. Shot 21, where an empty cup was used, attests to the desirable absence of a shock in the cup wall strong enough to initiate the MDF.

Table IX
TESTS AT 77°K

Shot. No.	Explosive	Velocity (mm/μsec) Stations					Average
		1-2	2-3	3-4	4-5	5-6	
45	Composition B Nitromethane	6.6	8.6	7.0	8.6	7.4	7.6
20		5.5	6.2	4.3			5.3
23		4.8	6.0	6.7			5.8
26		5.9	5.8	6.0			5.9
28		7.5	6.2	7.2	6.1	6.3	6.7
							Mean = 5.9

Table X
INERT MATERIALS TESTED AT 77°K

Test No.	Material	Results Velocity (mm/μsec) Stations				Remarks
		1-2	2-3	3-4	4-5	
24	Trichloroethylene	2.52	--	--	--	no record after Station 2
47	Liquid Nitrogen	--	--	--	--	no record
48	Liquid Nitrogen	--	--	--	--	no record
49	Liquid Nitrogen	--	--	--	--	no record

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No reliable values have been reported for the detonation velocity of Comp. B or nitromethane at 77°K (b.p. of liquid N₂). Our results are presented in Table IX where the value for Comp. B is consistent with an extrapolation from values presented by Malin *et al.*¹² Our values for nitromethane are all within 15% of the average. Thus at low temperatures this explosive witness method may be considered reliable to within 15%.

Since the test must distinguish between propagation and failure, the results of tests on inert materials are important (Table X). They indicate that tests on nondetonable systems will not give spurious results.

The precision of the method depends upon many factors including the care with which the components are aligned and the measurement made. The reproducibility with which the Primacord is initiated by a detonation is also important and at 77°K might prove troublesome. Experiments to initiate several pieces of Primacord simultaneously confirmed that the delay is small enough to have no significant effect upon the measurements.

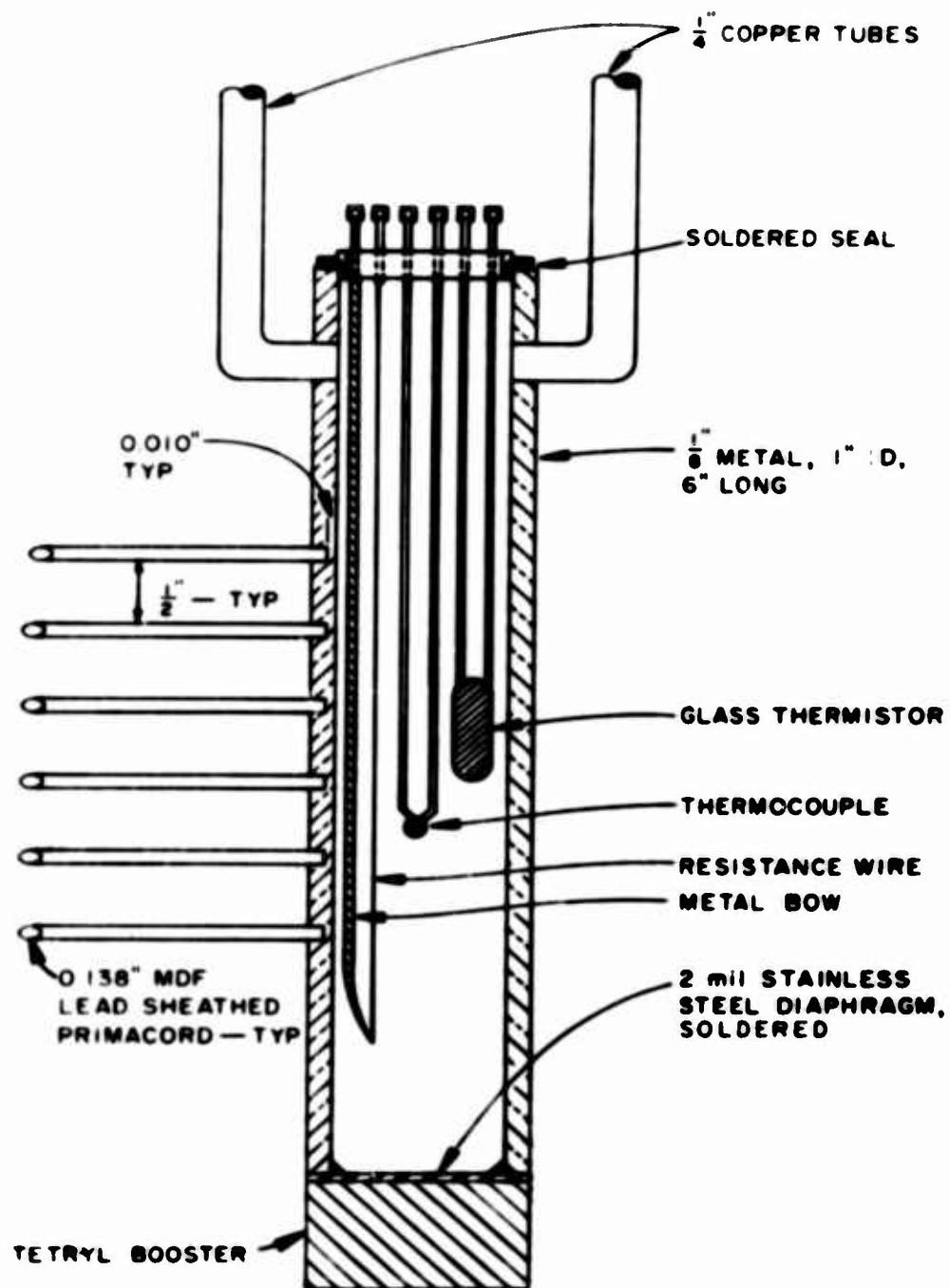
2. Resistance Wire--Constant Current Supply Method

This method, developed for solid explosives and adapted for liquids at ambient and low temperatures, is adequately described elsewhere.² The fine Nichrome resistance wire, attached to a constant current source senses the arrival of an ionization front from the detonation and immediately shorts to the wall of the cup. A recorded signal from this detonation front provides a continuous record of the disturbance.

3. Low Temperature Apparatus

Each cryogenic compound has properties which determine the design of confinement and transfer equipment. We have chosen to test perfluorohydrazine, N₂F₄, because it is toxic, corrosive, and possible detonable, yet available in quantities of reasonable purity needed for the test. These properties are probably representative of high energy oxidizers to be studied in later routine tests. For this material the cup was modified as shown in Fig. 22 to contain glass to metal seals at the top

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FIG. 22 CRYOGENIC TEST CUP DESIGN

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for thermistor leads, thermocouple leads (to aid in determining liquid level) and resistance wire leads. At the bottom of the cup thin, 2 mil, stainless steel diaphragms were silver soldered into place.

Vacuum transfer equipment, shown schematically in Fig. 23, was installed and remotely operated.

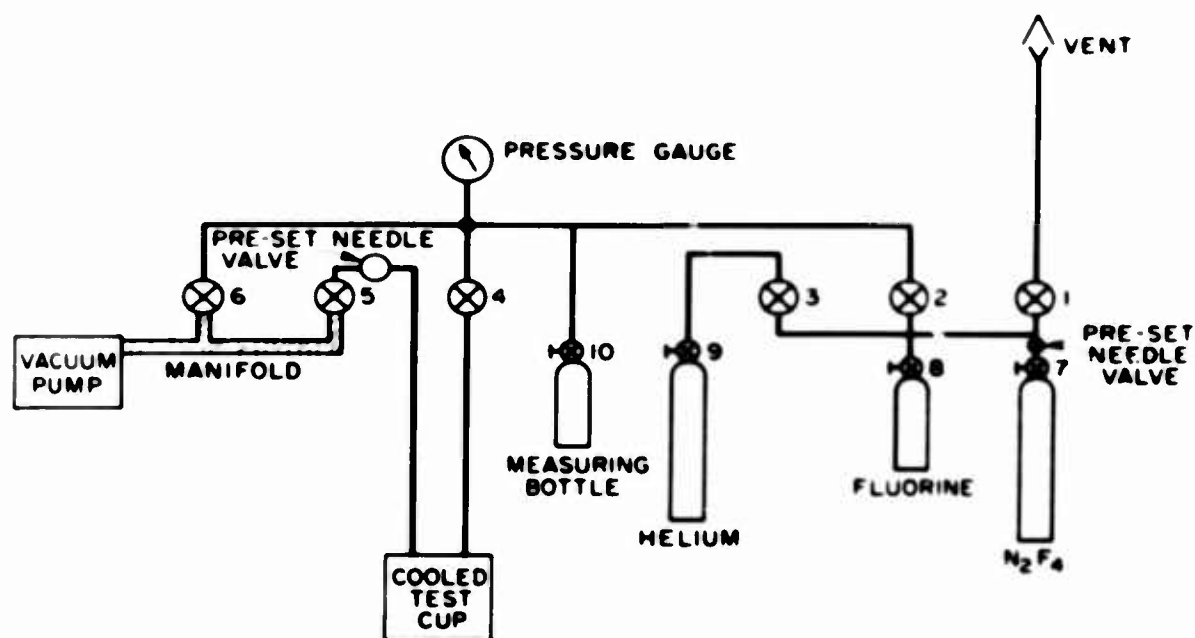


FIG. 23 SAMPLE HANDLING SYSTEM FOR CRYOGENIC TESTS

Cleaning--Some of the valves were found to have metal chips embedded in the Teflon gaskets. Therefore all valves were inspected upon receipt and the gaskets replaced where necessary. All components were cleaned for liquid oxygen service and, after assembly but just prior to use, the entire system was passivated with fluorine. The last operation was accomplished by evacuating the entire system with valves 1, 7 and 8 closed. Then, with valves 5 and 6 closed, fluorine was slowly admitted to the system through valve 8. (This procedure is recommended only for fluorine oxidizers.) Following passivation, valve 8 was closed and valve 1 opened. Valves 5 and 6 were then opened and the system cleared of residual fluorine.

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Components--Valves 7 and 10 were Chlorine Institute valves available from Superior Valve Co., Pittsburgh, Pennsylvania (Fluorine Cylinder Valve Cat. No. 1214F). Valves 8 and 9 are conventional as supplied by the vendor. All other valves are Hoke Cat. No. 30206-6 with No. 80065-1 solenoid. These are ball valves which operate more smoothly than conventional needle valves and thus are less likely to initiate an explosion in the valve. The vacuum pump is a conventional low capacity laboratory model filled with fluorocarbon oil but powdered with a 1 h.p. motor for easy starting. All transfer lines are copper tubing, silver soldered to valves and fittings. The test cup assembly is 1 inch Schedule 80 pipe, surrounded by a can cooled with dry ice.

Operating Procedure--To conduct a test, the apparatus was prepared as described, the detonation velocity instrumentation checked, the explosive components installed, and the coolant (solid CO_2 for N_2F_4) added. We found it convenient to assemble the apparatus with the test cup in a can (such as is generally used for 1 lb coffee) to contain the coolant for the short time needed. A typical test assembly is shown in Fig. 24. The remaining steps were conducted remotely as follows: With valves 1, 7, 8, and 9 closed, all others opened, evacuate system. Close all valves. Open valves 10, 7, and 2 in order. Fill measuring bottle to desired pressure as indicated on gauge. Close valve 2, then close valve 7. Open, in order, valves 1, 3, and 7. This flushes this section with helium and serves to isolate the supply tank from the measuring bottle. Open valve 4. Essentially all of the N_2F_4 in the measuring bottle should condense in the test cup. Completeness of condensation is adjudged with the thermistor (see Appendix B) and thermocouple liquid level detector. In this operation the test cup acts as a trap. Should any noncondensables interfere, they may be removed through the pump by briefly opening valve 5. The preset needle valve prevents surging or splashing of liquid. Close valve 4 and initiate test.

The procedure was to perform an initial test using Freon 12 to check operation of all tubing, valve, and gauges or monitoring devices. After this was done, nitromethane was tested. Then the experiment was immediately

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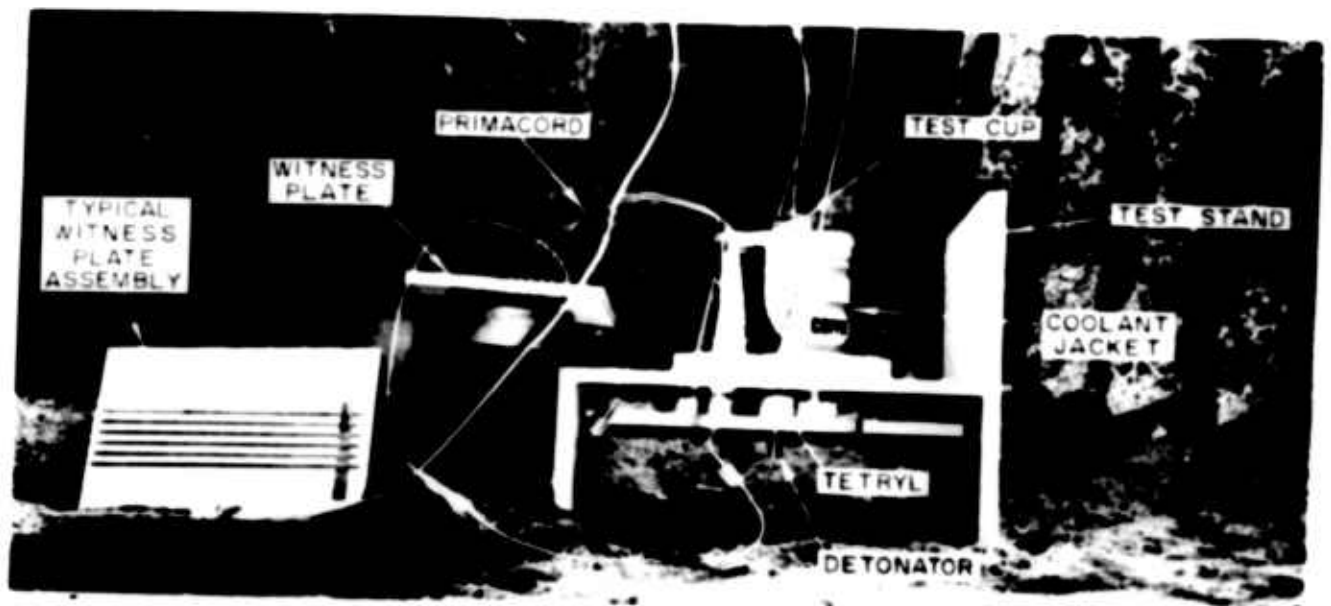


FIG. 24 TYPICAL CRYOGENIC TEST ASSEMBLY

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set up for N_2F_4 with no changes other than replacement of sample holder and leads destroyed in the previous test.

C. Results

A series of five shots with perfluorohydrazine was conveniently and successfully fired and Liquid N_2F_4 was found not to detonate at temperatures between -30 and $-40^\circ C$. These results were evidenced by failure to establish a conductive ionized reaction front in the resistance wire measurement, and by observation with the explosive probe system of an initial shock velocity of $2.8 \text{ mm}/\mu\text{sec}$ decaying to less than $1.5 \text{ mm}/\mu\text{sec}$ in a travel distance of 62 mm. (Five one-half inch intervals).

D. Conclusions

The modified Dautriche and the continuous wire methods function reliably, at ambient and low temperature conditions, to distinguish between detonating and non-detonating systems. Specifically, both techniques, used in conjunction with an appropriate sample handling system, establish that liquid perfluorohydrazine does not sustain a stable detonation.

There are some possible difficulties or objections to both systems. We have attempted to anticipate as many as possible. In some situations, the resistance wire and support may affect the behavior of the test material, e.g., the material may appear more sensitive than it is. Our experience indicates that if the wire is more than 2 inches from the booster the effect is not detectable.

The explosive probe system perturbs the test sample less but relies on accurate, reproducible assembly and behavior of high explosive materials when handled in the field by relatively inexperienced personnel and when detonated at a variety of temperatures. Our experience on this project has indicated that this is not a serious problem. The system may be less able to distinguish between stable detonations and those of slowly decaying velocity.

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We are confident that the general procedures described herein, suitably adapted for use with a particular chemical system, will reliably measure detonability at low temperatures.

E. Future Work

Essentially the same equipment (without a vacuum transfer line), will be used to study ethyl nitrate detonability characteristics at elevated pressures (150 psig) and temperatures, ca. 180°C. This will complete the tests and a test manual will be drafted.

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V PHYSICS AND CHEMISTRY OF DETONATION

(Joseph G. Berke, Marjorie W. Evans, L. B. Seely, D. Tegg)

A. Introduction

The objectives of this phase of the work on difluoroamino compounds originally were (1) to determine some of the detonation characteristics of these materials, and (2) to study the relationships between their decomposition kinetics and their failure diameters and shock sensitivities. The last annual report thoroughly reviewed failure diameter theory, and mapped the dependence of shock sensitivity and failure diameter on chemical and other properties for a range of assumed values of the parameters. Work during this year has been concerned with determining values of the quantities required by theory.

As work continued it soon became apparent that more and more sub-tasks should be included in the program. However, the scope of the work must be kept within bounds. We have, therefore, selected from among many topics those which either are absolutely necessary to the main objectives or seem likely to be especially fruitful. The following tasks are now being pursued:

1. Measuring and calculating detonation properties of difluoroamino compounds
2. Measuring failure diameters of difluoroamino compounds for both CJ detonations and low-velocity reaction waves
3. Studying the sequence of events during shock initiation in difluoroamino liquids and nitromethane; this information is also being used to evaluate the gap test and interpret shock sensitivity numbers
4. Measuring reaction times in difluoroamino liquids at temperatures and pressures comparable with those found in shocks
5. Measuring the equation of state of unreacted nitromethane and difluoroamino liquids as an adjunct to (4).

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B. Detonation Velocity of 1,2-DP

Since decomposition of difluoroamino compounds produces a large amount of energy, it can be almost a priori assumed that they will explode; however, at the start of this project it was regarded as an open question whether they would support a Chapman-Jouguet (CJ) detonation wave in ordinarily attainable diameters. The questions were: (1) Under what conditions will difluoroamino compounds detonate? (Are they sensitive or insensitive, and is their failure diameter small or large?), and (2) To what decomposition products should the CJ hypothesis be applied? (Does the reaction reach complete equilibrium at the CJ plane or is some process, such as precipitation of carbon, incomplete?).

A careful measurement by Lawrence Radiation Laboratory of the detonation velocity of 1,2-DP has been reported¹³ as 5.96 ± 0.05 mm/ μ sec. It seemed worthwhile to confirm this since (1) calculation had given significantly higher values, (2) measurement had been made only on one shot over two intervals along the charge, and (3) the explosive had been confined in copper, in which the velocity of sound is about 5 mm/ μ sec. The situation was confused by some of our own early evidence that 1,2-DP showed an unsteady wave with a velocity in the neighborhood of that of the steady one calculated for CJ conditions; this might have explained the discrepancy between the experimental and the calculated values. However, the apparent unsteady velocity has now been identified as an experimental effect and it is quite clear that 1,2-DP detonates steadily. Furthermore, it is believed that 1,2-DP behaves like other liquid explosives as far as the CJ detonation is concerned.

The experimental arrangement to measure the detonation velocity of 1,2-DP at one inch diameter is shown in Fig. 25. It was designed to yield a time-distance history over a fairly long run to assure reaching a steady velocity. For this reason timing signals were taken at eight stations starting 5 inches from the booster with insulated wires stretched across

¹³ Technical Progress Report 64-1, September 14 to December 14, 1963, pp. A-1 to A-10.

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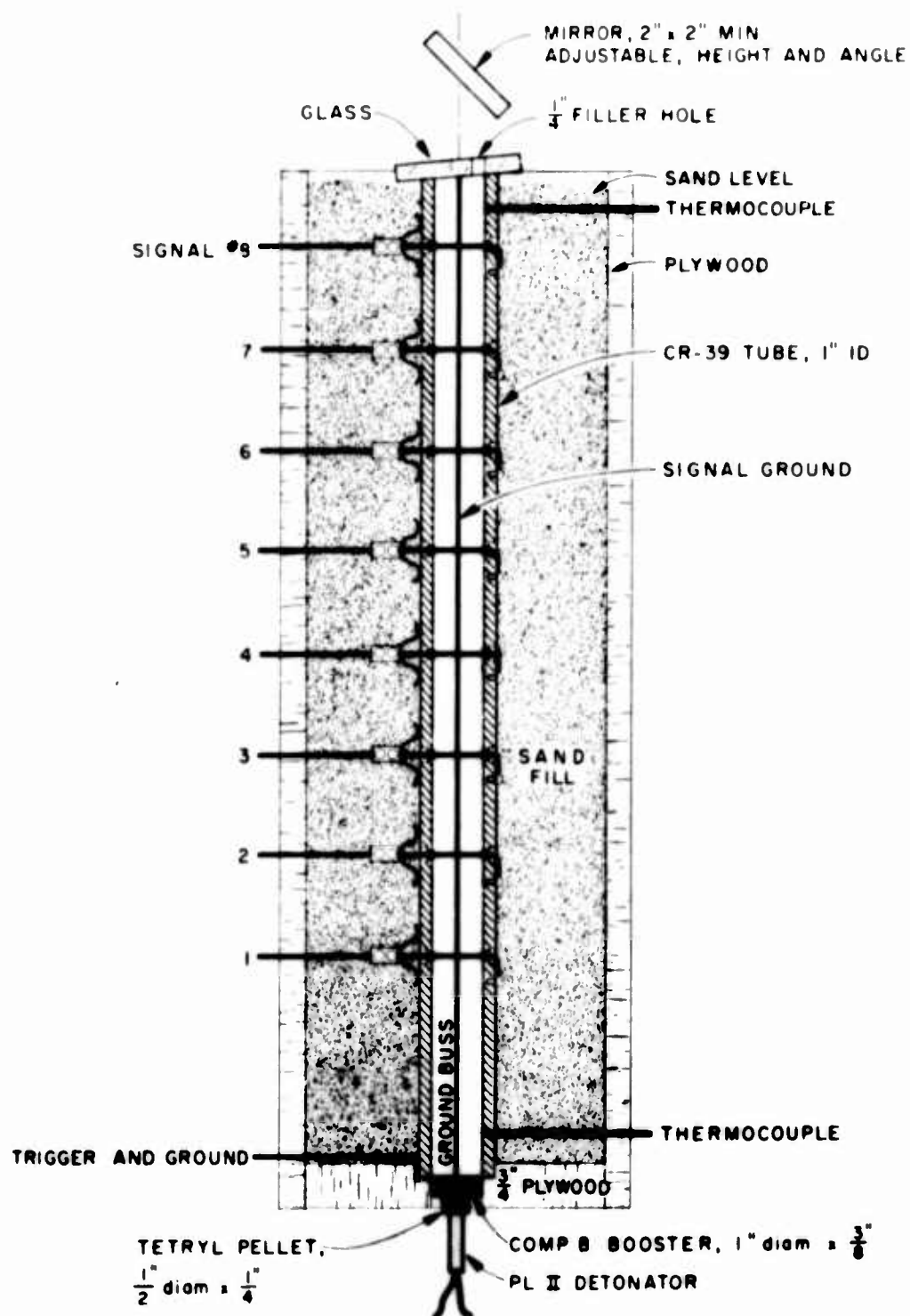


FIG. 25 CHARGE ARRANGEMENT USED FOR DETERMINATION OF THE DETONATION VELOCITY OF 1,2-DP

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the tube at 2 inch intervals. The signals were recorded by a raster oscilloscope (writing speed, 2-1/2 μ sec per line). The RMS deviation of these timing signals was estimated from the deviations of all the measurements about their appropriate averages, to be $\pm 0.017 \mu$ sec. The position of the wires was determined with a cathetometer to a precision of ± 0.1 mm.

Because many liquid explosives behave peculiarly in glass confinement, as evidenced by an anomalously large failure diameter and the presence of dark waves,¹⁴ the 1,2-DP was contained in a polycarbonate tube* 1 inch I.D. with 1/4 inch wall. In order to produce a high initial pressure the liquid was boosted with a Comp. B booster, 1 inch diameter by 3/8 inch thick, initiated at the center by a PL-2 detonator. Overboosting was prevented by the high wave curvature of the entering wave.

A normally occurring level of electrical conductivity in unshocked difluoroamino liquids makes it difficult to obtain good pin signals. Use of 0.005 inch enameled wire prevented conduction, but this immediately introduced two possible dangers: that the enamel would not break down sufficiently fast when the detonation wave passed; and that the wire would affect the structure of the detonation by producing dark waves. Consequently, a test shot was made in which a sample signal was recorded and the oncoming wave was observed with a smear camera as the wave collided with the wire. A sharp signal was obtained on the oscilloscope and no perturbations were seen on the smear camera record.

The firing tube was surrounded with sand to help maintain the temperature constant. Temperature was measured at top and bottom of the liquid column by means of thermocouples. The measurement of the wire spacings was carried out at 22°C and the shot was fired at 37°C. This temperature difference could result in a decrease in detonation velocity of 0.05 mm/ μ sec assuming a coefficient of expansion for 1,2-DP equal to that of nitromethane. The decrease due to increase in the wire spacings from expansion of the CR-39 would be less than 0.01 mm/ μ sec.

¹⁴ A. W. Campbell, T. E. Holland, M. E. Malin and T. P. Cotter, Jr., *Nature* **178**, 38 (1956).

*CR-39, obtained from Homalite Plastics, Wilmington, Del.

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The results of the test are given in Table XI. For the final velocity the estimated uncertainty has been increased arbitrarily from ± 0.02 mm/ μ sec, which would include deviations in the measurements over the last six intervals, to ± 0.05 mm/ μ sec, in view of the fact that only one shot was fired and to allow for possible systematic errors.

The sand around the charge was penetrated by a slot extending to the clear plastic wall of the firing tube along most of its length. The smear camera record obtained through this slot showed that the velocity was constant over most of the charge length; and it also gave an independent record of the velocity which is somewhat less precise than that obtained from the oscilloscopes.

The value of the detonation velocity $D = 5.89 \pm 0.05$ mm/ μ sec is in agreement with the value obtained at Lawrence Radiation Laboratory. Since the two measurements were by different experimental procedures, considerable confidence can be placed in the result. However, it is clear that the measured value of detonation velocity for 1,2-DP is lower than the 6.25 mm/ μ sec calculated with the RUBY code. A number of possible reasons for this have been suggested:

1. The measurements were made at 1 inch diameter and therefore the measured velocity is reduced by the diameter effect. In our opinion this explanation is unlikely. Liquid explosives exhibit only a small diameter effect^{11, 15} and until it is demonstrated otherwise, it should be assumed that 1,2-DP behaves like a normal liquid explosive in this respect.

2. The calculations have been made under the assumption of equilibrium, whereas it is more likely that some process like precipitation of carbon is incomplete. This may well be the case, but in most calculations such variations in products will not cause a 10% change in detonation velocity.

¹⁵ E. A. Igel and L. B. Seely, 2nd ONR Symposium on Detonation (ONR, U.S. Dept. of Navy, 1955), p. 321.

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Table XI

DETONATION VELOCITY OF 1,2-DP
SRI SHOT 10587

A. Oscilloscope Measurement

<u>Time, μsec</u>						
<u>Pin Station</u>	<u>Master</u>		<u>Slave</u>		<u>\bar{t}</u>	<u>σ</u>
	<u>1st Reading</u>	<u>2nd Reading</u>	<u>1st Reading</u>	<u>2nd Reading</u>		
1	0 ----arbitrary zero----				0	
2	8.73	8.72	8.69	8.70	8.71	
3	17.35	17.33	17.33	17.33	17.33	
4	26.00	26.00	25.95	25.96	25.98	
5	34.64	34.64	poor signal		34.64	± 0.017
6	43.26	43.26	43.24	43.26	43.26	
7	51.91	51.90	poor signal		51.90	
8	60.51	60.51	60.46	60.48	60.49	

DISTANCE AND INCREMENTAL VELOCITY

	<u>x, mm</u>	<u>Δx_{mm}</u>	<u>$\Delta t, \mu\text{sec}$</u>	<u>Dmm/μsec</u>
1	0	(arbitrary)		
2	51.2	51.2	8.71	5.88
3	103.0	51.8	8.64	6.00
4	154.0	51.0	8.63	5.91
5	204.8	50.8	8.66	5.87
6	255.6	50.8	8.62	5.89
7	306.5	50.9	8.64	5.89
8	357.2	50.7	8.60	5.90
				<u>5.89 \pm 0.05 mm/μsec</u>

B. Smear Camera Measurement

$$\theta = 79\frac{1}{4}^\circ \pm \frac{1}{4}^\circ \text{ at } 500 \text{ r.p.s.}$$

$$D = 5.89 \pm 0.13 \text{ mm}/\mu\text{sec}$$

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3. The detonation velocity is not calculated by the Ruby code accurately since this code has been adjusted empirically to fit CHON explosives. This seems to us a reasonable possibility. In view of the lack of experience with fluorine compounds in such calculations and the highly polar nature of HF, it may well be that the co-volumes and the equation of state of CF_4 and HF are not the correct ones. It is perhaps remarkable that calculated values have come as close to the measurements as they have. At present it is probably not profitable to make serious changes in the calculations. Only if it were possible to make very accurate velocity measurements of some fluorine-containing compounds over a range of densities and supplement these with CJ pressure measurements, could more suitable calculational constants be obtained. This would require relatively large quantities of a solid compound.

C. Failure Diameter of Domino Compounds

Before determining the failure diameter of a liquid explosive it is important to decide to what use the data will be put. If the interest in failure diameter arises from safety, the diameter to be determined is that below which strong shocks will cause no chemical reaction. Presumably the material could be handled with safety (as far as shocks are concerned) in pipes or vessels below that diameter. On the other hand, if the interest arises from theory, the diameter to be determined is that below which no Chapman-Jouguet detonation will propagate. There exists a theory¹⁶ for the failure of such waves, whereas low-order waves are not understood. Our present interest is mainly in the theoretical interpretation of failure diameters, and therefore in the minimum diameter for CJ detonations.

Since the conditions of test for these liquids were chosen entirely to facilitate theoretical interpretation and with no regard to the practical conditions of use, they may appear arbitrary and artificial in some respects. Thus, lead was used as the confining material because its

¹⁶ Marjorie W. Evans, J. Chem. Phys. 36, 193 (1962).

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sound velocity is very much lower than the full-strength detonation velocity of the difluoroamino compounds. It is obvious that lead is not a practical confinement material. By choosing lead, we hoped to avoid low-order waves supported by waves in the confining material but, after the fact, it is not clear we have been entirely successful in this.

The theory of failure diameter concerns the effect of flow divergence on the chemical reaction rate, and it is convenient to limit experiments to those in which the rate of divergence is held constant over the entire time during which the fate of the wave is being determined. Lead blocks rather than tubing were used because the thick walls make it unnecessary to consider the effect of shock reverberations. Use of relatively large pieces of lead had the added advantage that at small charge diameters they stayed in one piece under the disruptive force of the reaction, and thus served as their own witness blocks.

Although the concept of failure diameter is simple, a valid failure-diameter test is quite complicated. One set of difficulties centers on the problem of selecting the proper booster. An ideal failure diameter test would involve a very long charge so that the test section could be considered to be boosted by an identical section preceding it. If a very slight taper were incorporated in such a charge, failure would occur very close to the point on the taper at which the diameter became equal to the failure diameter. For such a very long charge the size of the booster would be of no importance provided it was large enough. In practice the length of hole that can be satisfactorily fabricated is limited, and it is thus of great importance to use the correct booster in order to save charge length. If the booster is too small, the explosive will fail no matter how large the diameter; if the booster is too large, the explosive will shoot below failure diameter through the limited length available. However, one may arrive at the correct booster by trying several sizes and determining over some small range of sizes, that the results do not depend on booster size. The preferred situation is to over-boost slightly using a column of the liquid sufficiently long that boosting effects can be shown to die out before the end of the column is reached. In spite of

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all precautions, complicated situations have been encountered with difluoroamino compounds, situations that apparently vary from isomer to isomer. It is important to proceed cautiously, with repeated checks on the booster effects under each new set of conditions and for each isomer.

In determining failure diameters of difluoroamino liquids in lead it has been found helpful to use as many effects as possible to aid in diagnosis of the results. First of all, the condition of the lead block after the explosion gives some indication of the nature of the disturbance in the liquid. That it is not a completely reliable indicator under all circumstances can be shown by firing a booster that is very much too large into water instead of into the reactive liquid. The resultant block looks somewhat like that produced by a reactive liquid when a smaller booster is used. Such a case is illustrated in Fig. 26. However, the conclusion that water has detonated should be avoided. In the more usual case, firing with a block filled with an inert liquid is quite helpful since the direct booster effects are indicated by the expansion of the block and the effect of reaction can be seen by comparison with a block fired with reactive liquid. Cases of this sort have been reproduced in the first quarterly report period of the current year.¹⁷ In general, comparison firings with an inert liquid is a second useful diagnostic result that is helpful in interpreting lead block failure diameter tests.

It has also been found useful to measure the transit times over the charge length used for the failure diameter test. It would be preferable to have a continuous record of wave velocity, but this is practically impossible at very small diameters. Even when the diameter is as large as 10 mm, it is difficult to measure the instantaneous velocity without either producing discontinuities in the wall or introducing inhomogeneities into the body of the liquid; either condition may change the results. The transit time measurements usually permit one to distinguish quite easily between full strength detonations (5 to 6 mm/ μ sec for these liquids) and

¹⁷ Technical Progress Report 64-3, March 15 to June 14, 1964.

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FIG. 26 SECTIONED 1 × 1-INCH LEAD BLOCK ORIGINALLY HAVING A 3.1 mm AXIAL HOLE AFTER FIRING WITH A 8.8 mm RDX PELLET AT DENSITY 1.6 g/cm^3 WHEN THE HOLE WAS FILLED ONLY WITH WATER.

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waves of lower velocity, if measurements over a number of charge lengths are made. However, a case in which electronic wave-speed measurements would be misleading was encountered while measuring slow waves. A two-inch round lead block containing water was fired with a 6.3 mm diameter RDX pellet at 1.6 g/cm³. The oscilloscopes apparently gave an average velocity of 2.7 mm/μsec. Again the conclusion that the water detonated should be avoided. In this case the state of the lead block recovered after firing, shown in Fig. 27, indicated the true state of affairs.

Another criterion of detonation which may be used to advantage in some cases is the temperature radiation from the products at CJ conditions. If a CJ detonation really exists, the products must eventually reach the full CJ temperature and for a clear liquid some temperature near this value should be recordable on a smear camera. Where the diameters being studied are very small, as in most of our failure diameter tests on DP compounds, such smear camera records are not practical; at diameters above 5 mm, they may be feasible.

Many difficulties in performing failure diameter tests on liquids derive from properties that are quite general among homogeneous explosives but are distinct from those of heterogeneous explosives. For instance, failure diameter for liquids is anomalously large in glass confinement and failure occurs by means of "dark waves."¹⁴ The failure diameter of a liquid explosive in metal (even a metal of low density) will be much smaller than in glass, and dark waves will not make their appearance except at discontinuities in the metal confinement. While there have been speculations as to the nature of these dark waves, they are not understood in detail, and the means by which they cause failure is not known. If we are to use failure diameter data to gain information on chemical reaction processes, it seems clear we must study failure occurring by smooth-flow divergence rather than via dark waves. Such considerations have dictated optimum conditions of test which in actual fact have been difficult to achieve in some cases.

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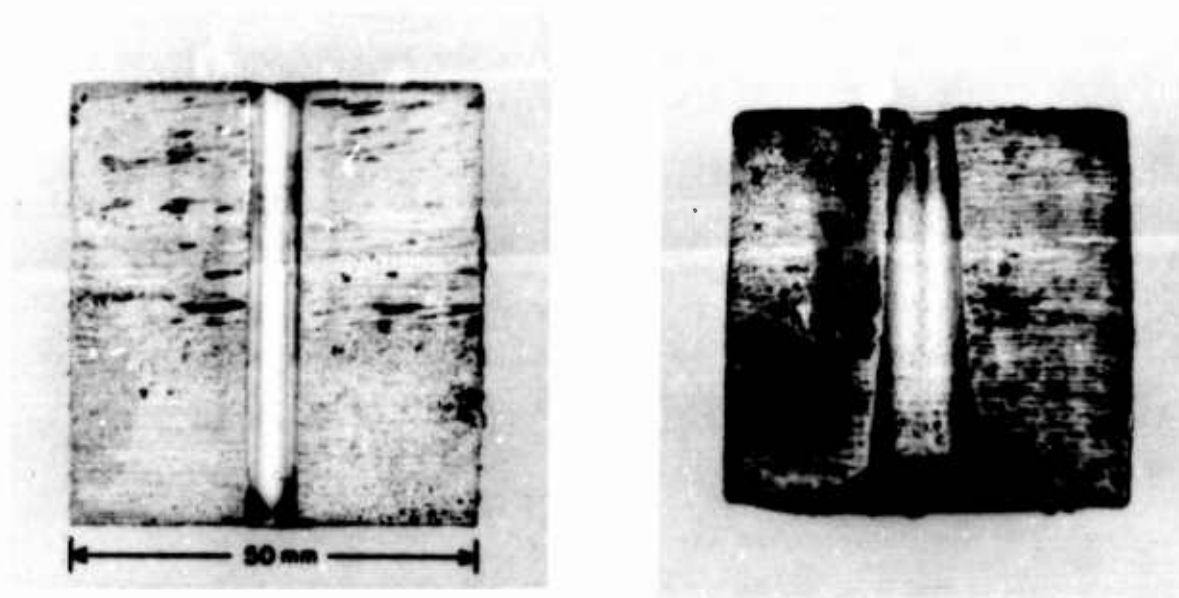


FIG. 27 A 2-INCH ROUND LEAD BLOCK BEFORE AND AFTER FIRING WITH A 12.5 mm diam. BY 6.3 mm THICK RDX PELLET AT DENSITY 1.60 g/cm^3

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For failure diameter tests we would suppose that holes in the confining medium must be fabricated with precision, since surface irregularities at the explosive-confinement interface are expected to produce failures. For instance, with nitromethane an abrupt increase in pipe diameter is used to prevent propagation of detonation through practical piping systems. For the difluoroamino compounds the exact quality of surface required to maintain detonation is not known. However, it was found that holes could be made in lead with a mirror-like finish. Consequently it was decided arbitrarily that no visible irregularities were to be accepted. The process of fabrication consisted in forcing a round-ended drill rod through the lead with a press. The flow of lead around the rod during pressing produced a smooth-surfaced hole, of the same diameter as the rod, and having no tendency to spring back. Since the yield strength of the lead is extremely low, we believe the lead around the hole may have been closer to its theoretical density than is usual in extruded blocks, but it seems unlikely that this method of making the holes would produce lead of anomalously high density. In Fig. 28 the sectioned 2-inch cube of lead on the left shows the quality of the surface inside a 6.3 mm hole. On the right is a similar block after firing

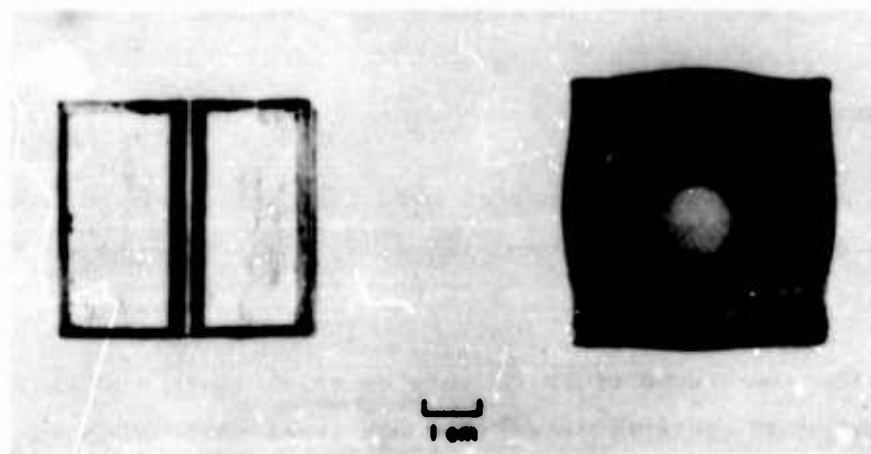


FIG. 28 TWO-INCH LEAD CUBE; ON THE LEFT SECTIONED TO SHOW THE INNER SURFACE OF A 1/4-INCH HOLE; ON THE RIGHT, A SIMILAR CUBE AFTER DETONATION OF 1,2-DP

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with 1,2-DP. Reasonably smooth straight holes have been made up to 125 mm long and down to 0.8 mm diameter. Below that diameter, the pressing pin wanders as it is pushed through the lead.

The results on failure diameters of domino liquids are still incomplete and it is therefore not appropriate to summarize or generalize the results in this annual report. However, the following conclusions from failure diameter tests in massive lead blocks appear valid:

1. In 1,2-DP, 2,2-DP, and IBA there are low-velocity reactive disturbances that will propagate in small diameters. At 0.8 mm diameter the wave has a velocity near 1.5 mm/ μ sec in 1,2-DP and 2,2-DP. In IBA, at 0.8 mm diameter, the wave propagates at velocities as low as 0.4 mm/ μ sec. These waves occur with heavy boosting. Failure diameter is below 0.8 mm for 1,2-DP and 2,2-DP, and very close to 0.8 mm for IBA.

2. There is a weaker wave in 1,2-DP that occurs at these same small diameters with weak boosting. The wave distorts lead less than the wave referred to above, but it is difficult to make measurements on.

3. The failure diameters of the CJ detonations (velocity above 5 mm/ μ sec) for these materials are somewhat larger than those for the waves referred to in item 1. For 1,2-DP the value is between 1.6 and 2.0 mm. For 2,2-DP the value seems to be just under 6 mm, but tests are not yet complete. The failure diameter for the fast wave in IBA appears to be above 6 mm.

4. All available diagnostic aids should be used in establishing a failure diameter, and care and ingenuity must be employed if confusing results are to be avoided.

5. Booster troubles in failure diameter tests indicate that a re-evaluation of the difluoroamino shock sensitivity data is necessary. We mistakenly assumed the booster proper for 1,2-DP would also be proper for 2,2-DP, but this is not the case, and it has caused us to confuse failures due to under-boosting with failures due to too small diameters.

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D. Measurement of Reaction Times in Shocks

In the last quarterly report we stated that relative reaction time measurements were feasible in shocked domino liquids and listed some preliminary values for 1,2-DP and IBA. It had already become clear that better control was necessary in the tests. Toward this end we have ordered 9404 pellets carefully quality controlled. Suitability tests have shown that the attenuators can be made of CR-39 rather than of Plexiglas, and techniques for determining the pressures in this new material in the gap test geometry have been developed. Methods have also been developed for more precise assembly of components.

It was also mentioned in the last quarterly report that nitromethane would be investigated rather thoroughly both as an example of a well-known liquid whose initiation characteristics have been studied and as a material on which technique studies may be made without wasting more valuable materials.

A number of shots have been fired with nitromethane in the way described in the last quarterly report. The charge arrangement is shown in Fig. 29. As in the case of the difluoroamino liquids, nitromethane also was initiated at the walls in many cases. Figure 30 shows two smear camera pictures of nitromethane fired in gap-test geometry in lead and polyvinyl chloride containers. In lead the detonation starts early at the wall and propagates to the center without central initiation zones being visible. A number of details seen there have not been explained. In the case of the polyvinyl chloride container, detonation also starts at the wall but there is some evidence of reaction in the original shock before the waves from the side meet at the center. A number of failure waves are visible close to the walls.

In order to obtain reaction time data on difluoroamino liquids or nitromethane it will be necessary to vary the attenuator thickness, i.e., the peak pressure of the entering shock. At some or perhaps all of these pressures, detonations from the walls may prevent seeing the reaction zone. It has therefore become clear that wall effects should

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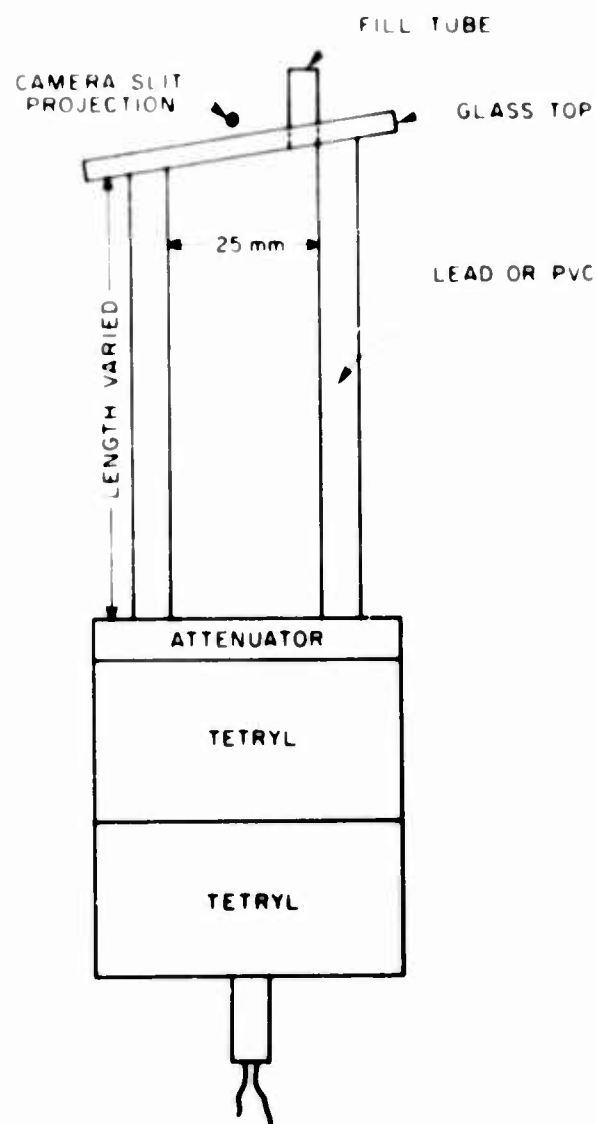
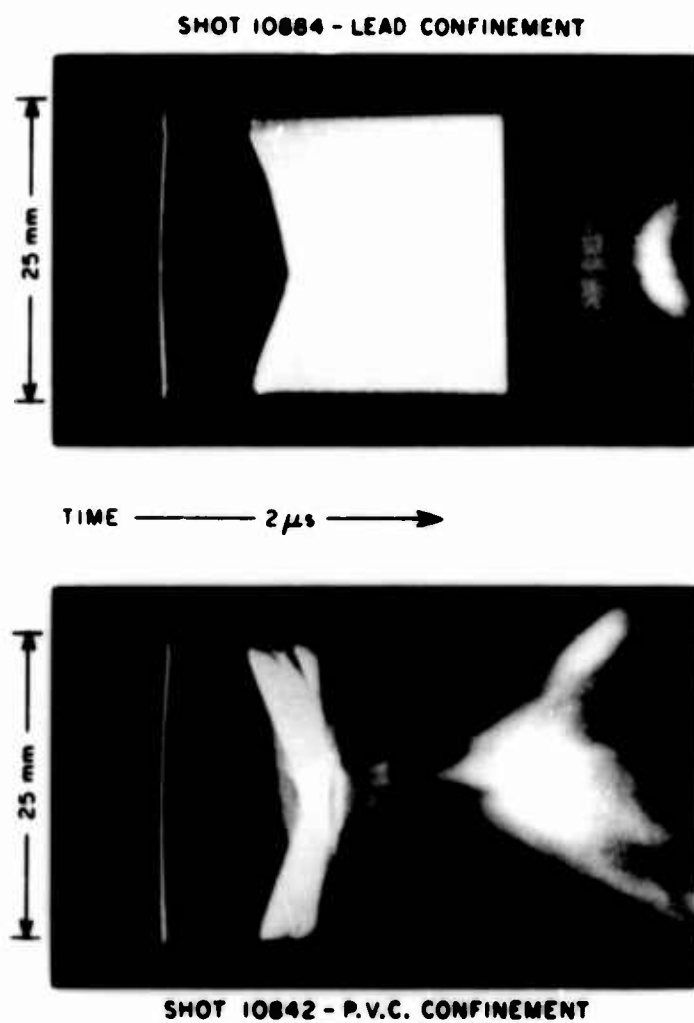


FIG. 29 CHARGE ARRANGEMENT USED IN OBSERVING INITIATION WITH THE SMEAR CAMERA

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**FIG. 30 SMEAR CAMERA RECORDS OF
INITIATION OF NITROMETHANE**

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be eliminated. This can be accomplished in the case of nitromethane by using a large container. For less plentiful compounds a matched-wall container should be used. We have started to work out the techniques for developing such containers using nitromethane as a trial material.

Figure 31 shows smear camera records of initiation phenomena in nitromethane in 3-inch square boxes. Here the walls were far enough removed from the edge of the boosters so that no initiation took place at the walls, and for all strengths of shock we can see initiation taking place in the entering shock without interference. In the case of the 1.6 mm attenuator, the shock produced detonation almost immediately upon entering the nitromethane. The detonation was overdriven directly by the original shock. With the 3.1 mm attenuator there is some evidence of a reaction time and a very narrow overtake zone. For the 4.7 mm attenuator the reaction times and the overtake zone are measurable. The new detonation is overdriven at breakthrough. At 6.3 mm both zones are larger and at 7.9 mm larger still. Measurements from these films are given in Table XII.

As a result of these experiments and others like them we have concluded that a serious perturbation arises from the granularity of the tetryl. (Compare the granularity of the booster flashes in Figs. 31a and 31c with irregularities in the initiation trace.) We have also concluded that the plastic CR-39 (polydiethyleneglycol bis-allyl carbonate) is a satisfactory attenuator. It does not require protection from nitromethane or difluoroamino liquids. The asymmetry in Fig. 31d is unexplained, but appears with a slightly different shape in two shots at this attenuator thickness. Perhaps this can be avoided by extreme care in assembly of the charge and explosive container. This series of shots will be repeated with better control.

While wall effects can be avoided for nitromethane by using a large container, tests of difluoroamino liquids must be run on smaller quantities. Figure 32 shows a container design in which the wall consists of 0.001 inch thick Mylar surrounded outside by a non-explosive compound

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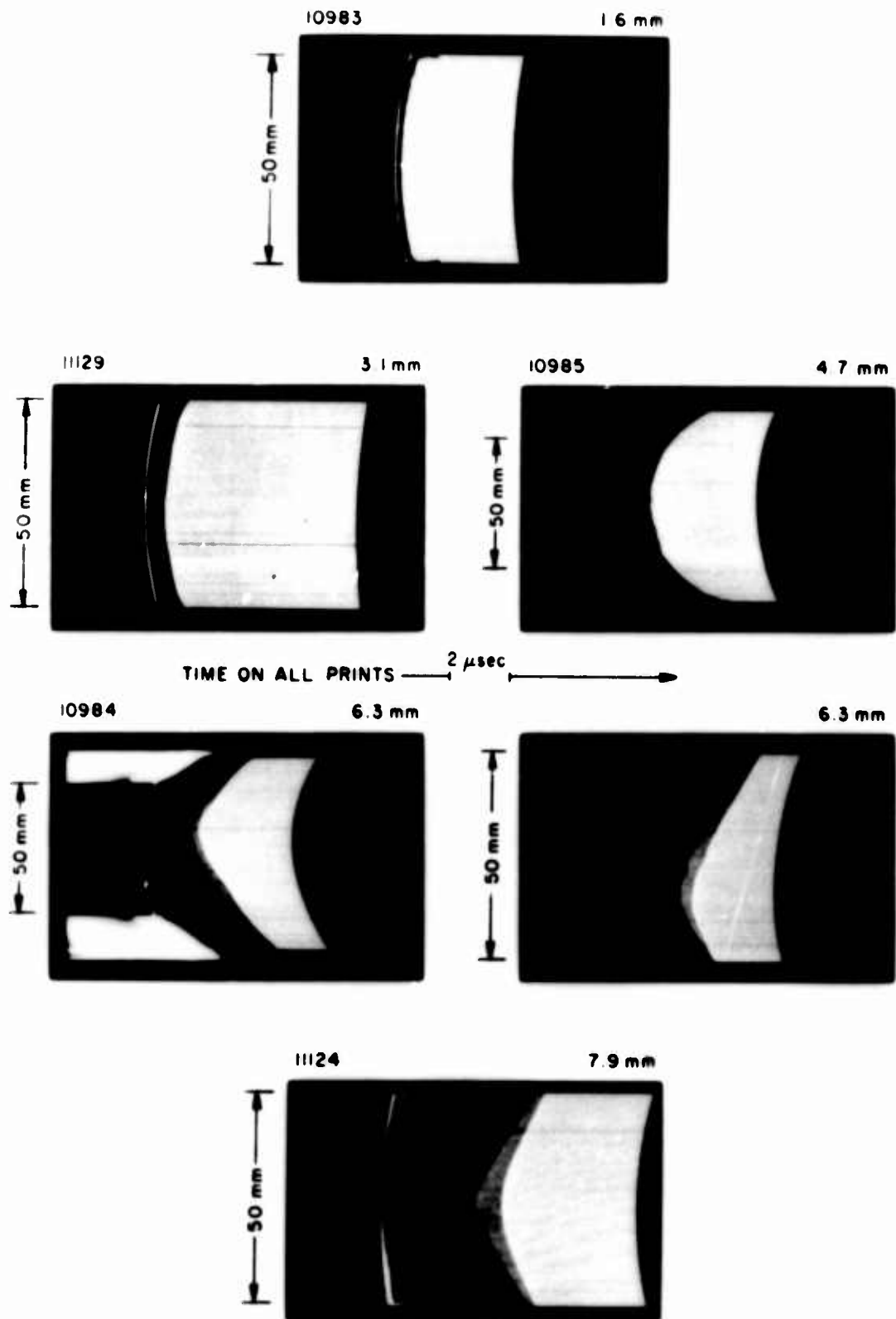
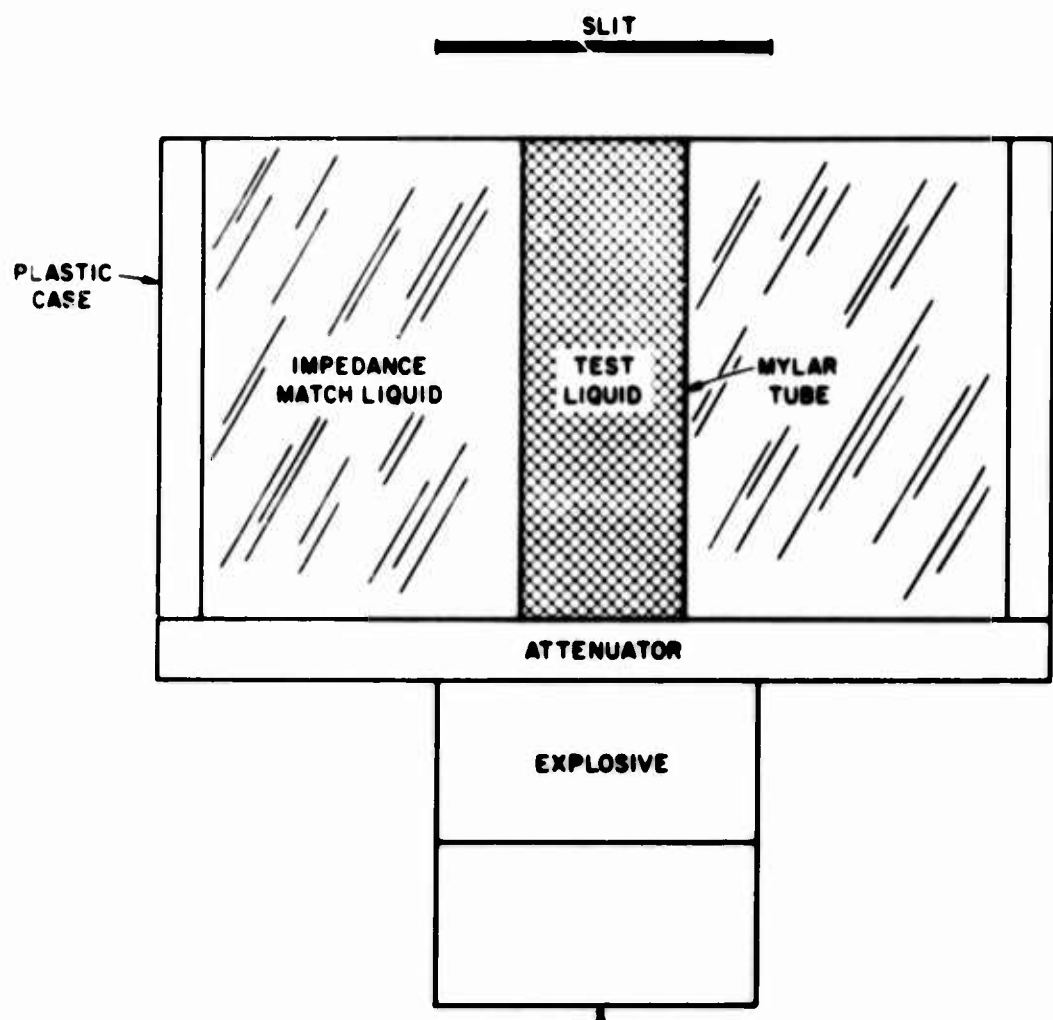


FIG. 31 SMEAR CAMERA RECORDS OF INITIATION OF NITROMETHANE
IN 3-INCH SQUARE BOXES OF CR-39

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FIG. 32 PROPOSAL DESIGN FOR "WALL-LESS" CONTAINER

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Table XII

PRELIMINARY INITIATION DATA ON NITROMETHANE

Shot Number	Attenuator Thickness mm	Estimated* Reaction Time μsec	Overtake** Time μsec
10,983	1.6	0	0
11,129	3.1	0	0
10,872	4.7	0.32	0.19
10,985	4.7	0.35	0.19
11,128	6.3	0.9	0.4
10,984	6.3	1.2	0.5
10,986	6.3	1.6	0.8
11,126	7.9	2.0	0.9
11,124	7.9	3.3	1.6

*These times are called estimates because the entry times into the liquid are not recorded on these films but were obtained in another series of shots on a similar but not identical plastic attenuator.

**Time from the first emission of reaction light until the newly initiated detonation overtakes the original shock.

that matches the explosive liquid on the inside. In order to choose a suitable liquid we must determine the Hugoniot curves for the explosives and for the inert liquids and see that they match in the range of shock strengths to be studied. Successful tests have been run to determine the unreactive Hugoniot of nitromethane. A matched liquid will be selected and reaction times for nitromethane measured in matched-wall containers. If the times determined on the small samples agree with those determined on the large samples the same techniques will be applied to difluoroamino compounds. This will require determination of the Hugoniots of difluoroamino compounds which we are prepared to do on small samples.

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E. Future Work

The tasks to be completed on this phase of the program are as follows:

1. Complete the determination of the failure diameters of 2,2-DP and IBA in massive lead confinement
2. Determine failure diameters of 1,1-DP, 1,3-DP, and 2,3-DB
3. Determine reaction times of other difluoroamino compounds:
 - a. The equation of state of CR-39 and calibration of the test geometry
 - b. The Hugoniot of nitromethane and as many of the six available difluoroamino compounds as time permits
 - c. Estimation of shock sensitivity of these compounds in the matched-wall arrangement
4. Estimation of the temperatures of shocked liquids
5. Correlation of data in terms of the theory of failure diameter.

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VI DECOMPOSITION OF NF COMPOUNDS

A. Low Pressure Pyrolysis Studies of Compounds 1,2-DP and 2,2-DP (S. W. Benson, G. N. Spokes)

1. Introduction

The results of experiments on the decomposition of difluoroamino substituted hydrocarbons have proven difficult to unravel. The following approaches have been used:

1. Pyrolysis of the gases followed by product analysis
2. Pyrolysis of the liquid and of solutions in nitrobenzene, toluene, methanol, etc., followed by product analysis
3. Investigation of the effects of various substances as reaction catalysts.

From these patiently pursued experiments much useful data have emerged. However, it has been found that the experiments are plagued with (a) wall-catalyzed effects even in "seasoned" vessels, (b) autocatalysis by the reaction products, and (c) secondary reactions which lead to tar formation and perhaps loss of important product molecules.

Experiments reported under this section have chiefly dealt with the compounds 1,2-DP and 2,2-DP.

2. 1,2-DP

Analysis of decomposition products of this compound has shown the presence of $\text{CH}_3\text{-CNF-CN}$ (known as NFP) and CH_3CN plus polymeric residue.¹⁸⁻²¹ HF production autocatalyzes the self-decomposition.²¹ Most surfaces

¹⁸ First Annual Report, March 15, 1962 - March 14, 1963, p. 33.

¹⁹ Technical Progress Report 63-1, March 15 - June 14, 1963, p. 7.

²⁰ Technical Progress Report 63-2, June 15 - Sept. 14, 1963, p. 17.

²¹ Technical Progress Report 64-1, Sept. 15 - Dec. 14, 1963, p. 25.

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catalyze the decomposition.²¹ Tar formation is suppressed by HCl, although HCl does catalyze the decomposition. In the temperature range 165-200°C in nitrobenzene 1,2-DP is ten times as reactive as 2,2-DP. The 1,2-DP decomposition rate appears²² to be $3.7 \times 10^{14} \exp (-40/RT)$.

In methanol at 50°C both HCl and LiCl enhanced the decomposition rate; hence the catalytic action is believed to be anionic rather than acid.²³

3. 2,2-DP

The thermal decomposition of 2,2-DP in nitrobenzene also yielded acetonitrile, and large amounts of polymeric residues. This suggests that HF elimination is important even for this compound. The rate for 2,2-DP was found to be lower than that for 1,2-DP. HF production autocatalyzes the self-decomposition of bulk 2,2-DP.²¹ NaF and KF suppress the decomposition.²¹ There is some doubt about the identity of other products of thermal decomposition of 2,2-DP.

4. Low Pressure Pyrolysis

Interpretation of results of experiments on the pyrolysis of gaseous compounds under the usual conditions of temperature and pressure is often difficult. The reason is that fragments formed from the first molecular breakup (initiation process) will continue to react in a free-radical chain process until a termination step occurs. It is often impossible to identify the initial step by analysis of the products or by other standard chemical procedures.

However, if experiments could be conducted at such a low pressure that analysis of products could be done before the fragments reacted, then the initiating steps could be immediately elucidated. This is the nub of the principle of low pressure pyrolysis, which is applied here to a study of 1,2-DP.

²² Reference 1, p. 5.

²³ Technical Progress Report 64-3, March 15 - June 14, 1964, p. 26.

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Cold gas is admitted to a fused silica furnace in which some degree of temperature accommodation takes place. We expect fast translational and rotational energy accommodation (5 to 10 collisions) followed by rather slower vibrational energy accommodation (tens of collisions). When the molecule accumulates enough internal energy for decomposition to occur, then--since there are no stabilizing collisions (in contrast to the higher pressure case)--the molecule will decay to fragments. The fragments, stable with respect to temperature, will pass from the vessel into the mass spectrometer without further reaction.

a. Theory

Translational and rotational energies, even though they accommodate quickly, make little or no contribution to the total molecular energy. It is on the vibrational energy of the molecules that we must focus attention since a typical molecule will have* skT of energy (compared with only $3/2 kT$ in translation of $3/2 kT$ in rotations) and may be an appreciable fraction of the activation energy E_a if $s \sim 20$ or 30 and $T \sim 800^\circ K$.

The precise nature of the interaction between molecule and wall will be highly complex, for the slowly rotating molecule may be expected to "impact" at several different points before departing. The chances of sticking can be estimated to be small at high wall temperatures. The residence time of a "stuck" molecule may be only a few tens of molecular vibration times. If during this time, however, the molecule can be decomposed as in a metathetical reaction, some perturbation of the results would be expected. We expect to be able to separate such effects from noncatalyzed decomposition by varying the character of the walls.

The average time taken for a molecule to acquire an energy E is given approximately by

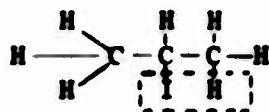
$$1/t \sim \frac{Z}{(s-1)!} \left(\frac{E}{RT}\right)^{s-1} e^{-E/RT} \quad (1)$$

where Z is the number of collisions/sec the molecule makes with the wall.

* s is the number of active oscillators in the molecule.

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In a molecule such as 1-propyl iodide, for example



the elimination of HI requires a total of 43 kcal in the appropriate C-I and C-H bonds.

The very simple, classical theory of unimolecular reactions predicts that for a molecule like 1- $\text{C}_3\text{H}_7\text{I}$ to decompose in from 10^{-4} to 10^{-5} sec, it will have had to have obtained about 21 kcal of internal energy in excess of the activation energy E_0 required to split out HI at "high" pressures. Hence $E = 43 + 21 = 64$ kcal. From Eq. (1) we see that the total number of wall collisions, Z_w to do this at 1000°K is:

$$Z_w = 1000 \text{ collisions.}$$

This has been independently confirmed by experiments with 1- $\text{C}_3\text{H}_7\text{I}$. Thermodynamics cannot tell us what the vibrational energy accommodation rates are. We can only know that a molecule with energy in excess of $(s-1)kT$ will tend to lose energy and one with less energy will tend to gain energy. We cannot, however, know from theory the magnitude of this tendency.

Experiments are not so handicapped. The variables at our disposition are the temperature T , the collision number Z , and the nature of the wall.

Let us briefly consider the expected amount of decomposition as a function of number of collisions at fixed temperature.

If $E_0 \sim sRT$ then we do not expect a significant amount of reaction until Z_w is at least of the order of s . As Z_w increases, the amount of reaction will increase. From the threshold and slope of the curve of % reaction versus Z_w we will be able to determine details of the energy accommodation between molecule and surface.

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Variation of vessel temperature will permit determination of the activation energy.

Further obvious experiments suggest themselves.

1. Addition of an inert carrier gas to give enhanced and controllable number of collisions
2. Variation of reactant pressure to study reactions between product and reactant molecules
3. Variation of wall material to study the effects of catalytic walls.

b. Experimental

A general schematic of the apparatus is pictured in Fig. 33. Cold gas passes through a needle valve to the fused silica collision chamber. After approximately 100 collisions the molecules pass into the mass spectrometer and are then pumped away by a fast diffusion pump. Gas pressure in the spectrometer (as measured by an ion gauge) is kept below 5×10^{-5} Torr. The mass spectrum does not depend on spectrometer chamber pressure in the range of 0.5×10^{-5} to 5×10^{-5} Torr. The gas pressure in the "reactor" may be fifty times the pressure measured by ion gauge.

The apparatus consists of four main sections: the gas handling system; the collision chamber furnace and furnace power supplies; the quadrupole mass spectrometer and its associated electronics, including detection and recording apparatus; and the vacuum system for the spectrometer.

Gas Handling System--The gas handling system has been made simple. Explosion hazards are minimized by keeping the gases confined to a small part of the system. The dead space between the spectrometer inlet valve and the sample bottle's bellows valve is evacuated simply by opening the inlet valve.

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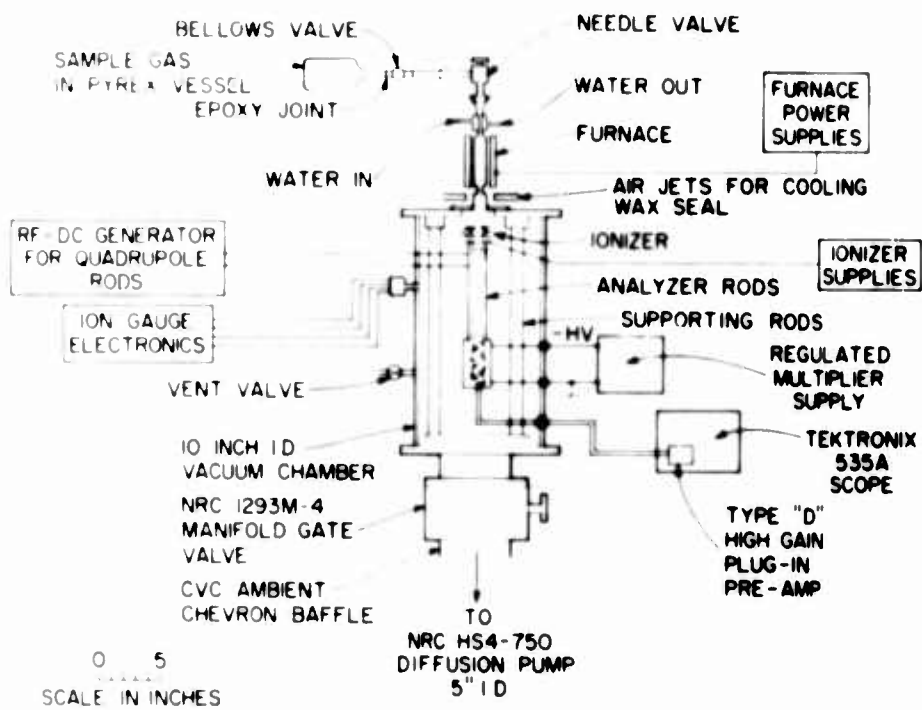


FIG. 33 GENERAL SCHEMATIC OF LOW PRESSURE PYROLYSIS APPARATUS

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The Collision Chamber--Again a simple design has been adhered to (see Fig. 34). The chamber was made from fused silica by an SRI glassblower. The gas supply tube is water-cooled in order to ensure a steep temperature gradient near the entrance to the furnace. The gas passes down a capillary into the furnace. A gas baffle obstructs the passage of the gas emerging from the capillary. Very little reacted gas can flow back up the capillary. The gas molecules impact with the walls, the approximate collision number being given by Z_w where

$$Z_w = \frac{\text{Total internal surface area of vessel}}{\text{Area of exit aperture}}$$

The collision chamber is heated by a pair of 4-inch-long "clam shell" heaters which supply the bulk of the heating power. A pair of small Nichrome elements are located near the top and the bottom of this furnace and permit the temperature to be made uniform (within 5°C) up to 1000°C. Temperature is monitored at 6 points using chromel-alumel thermocouples.

The Quadrupole Mass Spectrometer--A quadrupole mass spectrometer has been used for these studies (see Fig. 35). (The device is described in Ref. 24). Spectra have been scanned at frequencies 3.5 and 2.7 Mcs with a voltage sweep to cover the mass ranges 5-76 and 10-150. When the instrument is in good adjustment, unit masses can be separated at up to 150 AMU. Quantitative reproducibility and sensitivity leave something to be desired however. The quadrupole spectrum is linear with applied voltage. This makes peak identification relatively easy.

The output from the particle multiplier is taken directly into the preamplifier of a Tektronix 535 A oscilloscope. Photographs of the screen are taken with a Polaroid camera. Measurements of the positive film are made using a Telereadex film reader. The pictures are rendered translucent with a compound called "No Scratch."^{*}

²⁴ "Quadrupole Mass Spectrometers," Philip Rice, Stanford Research Institute. First Interim Report on Contract DA-44-009-ENG-5127, 30 April 1963. AD 407494-L.

^{*} Manufactured by Edwal Scientific Corporation, Chicago, Illinois.

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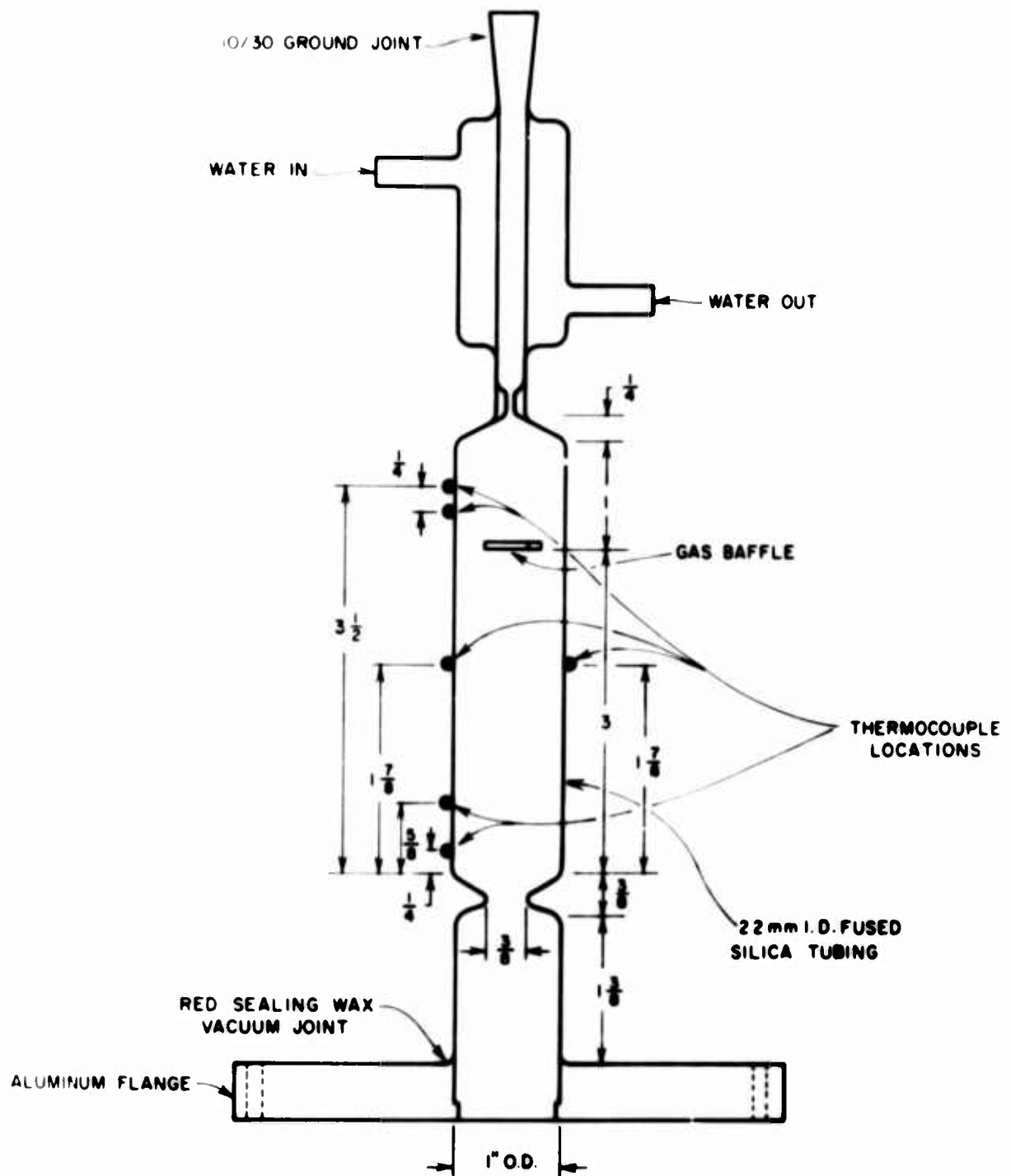


FIG. 34 FUSED SILICA COLLISION CHAMBER

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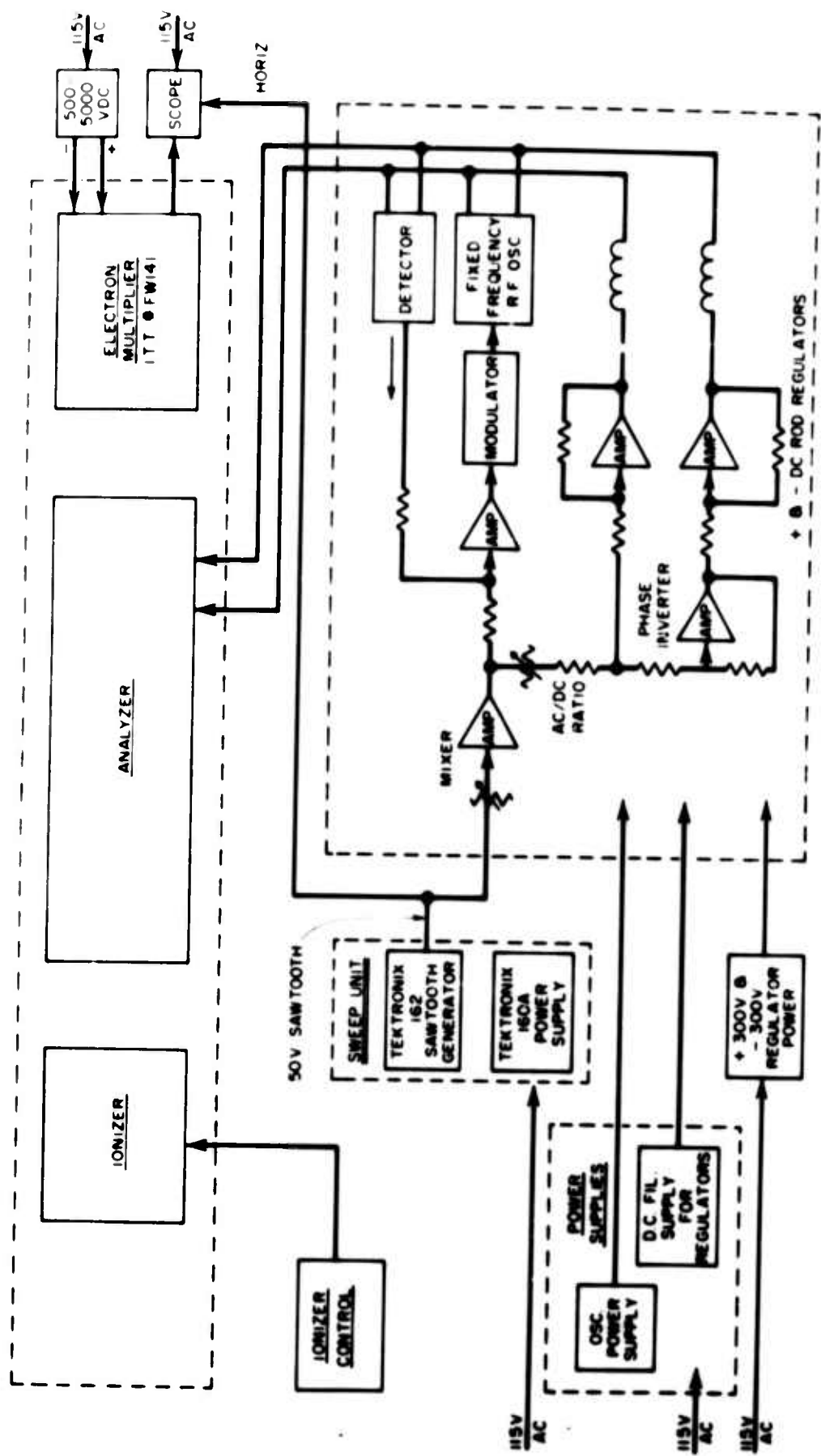


FIG. 35 MASS SPECTROMETER ELECTRONICS BLOCK DIAGRAM

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The Vacuum System--The spectrometer is housed in a 10 inch ID aluminum vacuum vessel. A 5 inch diameter diffusion pump (NCR type HS4-750), cold baffle, and Tamescal manifold gate valve are used. A small 1 inch diameter booster diffusion pump (not shown in the diagram) ensures a low fore pressure for the main diffusion pump.

c. Results

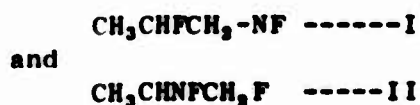
Experiments on the low pressure pyrolysis of 1,2-DP have been started and preliminary results obtained.

Decomposition begins at about 600°C in our 100-collision vessel. It is about 50% at 700°C. At 900°, decomposition is essentially complete.

Mass peaks prominent in the parent molecule are found at 47 and 66. As decomposition proceeds these peaks drop to a small height and new ones at 33 and 52 AMU become prominent. Mass 20 also becomes more evident.

The chief decomposition mechanisms which we have considered are:

- (1) NF_2 elimination followed by a second NF_2 elimination; products are simply propylene and NF_2 molecules
- (2) NF_2 elimination followed by a cyclic transition state rearrangement of the fluorines to give the molecules



The extra energy acquired from the rearrangement will make the radical I unstable and lead to products $\text{CH}_3\text{-CHF}$ and $\text{H}_2\text{C} = \text{NF}$. Similarly, II will decompose to $\text{CH}_3\text{CH} = \text{NF} + \text{CH}_2\text{F}$ or $\text{CH}_2\text{FCH} = \text{NF} = \text{CH}_2$; these products may further decompose to $\text{CH}_3\text{CN} + \text{HF}$ or to $\text{CH}_2\text{FCN} + \text{HF}$.

- (3) HF elimination to give $\text{CH}_3\text{CNFCH}_2\text{NF}_2$, III, or the isomer $\text{CH}_3\text{CHNF}_2\text{CHNF}$, IV. These molecules may undergo further HF elimination to give, as products, $\text{CH}_3\text{CNFCHNF}$ or even CH_3CNPCN from III and $\text{CH}_3\text{CHNF}_2\text{CN}$ and CH_3CNPCN from IV.
- (4) Other routes such as successive HF, NF_2 eliminations will be considered if future evidence should so demand.

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While we have accumulated a considerable amount of data on 1,2-DP, they have not been completely analyzed owing to lack of fragmentation patterns of intermediate compounds and product species. The same is true of 2,2-DP, although we have fewer data for this compound.

However, preliminary inspection of the data indicates the following to be true:

- (1) 2,2-DP decomposes faster than 1,2-DP in our system
- (2) Decomposition of 1,2-DP gives as one of the major reaction paths, $C_3H_6 + 2NF_3$.
- (3) Most of the main features of the 1,2-DP decomposition can be accounted for by assuming an initial NF_3 split out followed by a rearrangement as already described.
- (4) There is no evidence for catalytic decomposition of either compound on the quartz walls.

B. Decomposition in Solution

(David Ross, Theodore Mill, Marion Hill)

1. Introduction

The decomposition of 1,2-DP was initially studied at 150-200° and was made on the neat liquid or a solution of the material in an aprotic solvent such as nitrobenzene. The decomposition yielded as the major volatile product 2-(N-fluoroimino)-propionitrile (NFP), formed by the loss of three molecules of HF from 1,2-DP. The substrate initially disappeared with a first-order half-life of about 19 hours. However, after 3 to 4 hours, the decomposition became autocatalytic. The autocatalysis was suppressed by addition of sodium fluoride. The initial disappearance of 1,2-DP was markedly accelerated by the addition of HF and HCl as well as KF, glass wool, and Teflon.

IBA, 1,3-DP, and 2,2-DP were studied in a similar manner. In all cases autocatalysis was suppressed by addition of sodium fluoride. The relative instability of the NF_3 compounds studied at 176° is 1,2-DP < IBA < 1,3-DP < 2,2-DP with relative rates of decomposition in the ratio 10:3:3:1.

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2. Decomposition Studies at 50°

a. 1,2-DP--The studies discussed above suggest that the decomposition of NF_2 compounds proceeds through successive dehydrofluorinations catalyzed by either acid, base, or both. The nature of this catalysis has been determined through a series of experiments at 50° in protic solvents. The decomposition of 1,2-DP was found to proceed at a reasonable rate under these conditions.

The disappearance of 1,2-DP and simultaneous formation of NFP in methanol, followed semiquantitatively by gas chromatography, had a half-life of several days. The reaction was accelerated five- to ten-fold by both added neutral salts, such as LiCl and LiClO_4 , and acids, HCl and H_2SO_4 .

A method was developed for quantitatively following the rate of decomposition of NF_2 compounds. The reactions were carried out at 50° in 90% water-10% dioxane and the progress of the reaction determined by periodically withdrawing aliquots and titrating for liberated fluoride. Fairly good first-order plots were obtained to better than two half-lives. Thus far, only data on 1,2-DP are available. The concentration of substrate in these runs was on the order of 10^{-2} to 10^{-3} M. No autocatalysis was observed and NFP was the sole product. The results, tabulated in Table XIII, show that no acid catalysis took place. A detailed discussion of these results appears below.

One difficulty experienced in this kinetic work was that at the completion of reaction, the concentration of fluoride ion corresponded to about two molecules of HF liberated per 1,2-DP molecule. (NFP was the only product observed.) The formation of NFP from 1,2-DP requires, of course, the loss of three molecules of HF. Studies of the F^{19} NMR spectra of the reaction mixture showed, in addition to peaks from the products NFP and HF, a multiplet at + 151 ppm from CFCl_3 . This same multiplet, in addition to a peak for HF, was observed in the F^{19} NMR of a 10% solution of HF in a glass NMR tube. The signal at + 151 ppm

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Table XIII^a

DECOMPOSITION OF 1,2-DP in 90% WATER-10% DIOXANE AT 50°

Conditions	$k_{\text{obs}} \times 10^4 \text{ (sec}^{-1}\text{)}$
1.96M HCl	1.33, 1.43, 1.46 ^{b, c}
1.97M DCl	1.07 ($k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = 1.32$)
2M NaCl	1.05
2M KF	fast ^d
No acids nor salts added	1.29

^aThe concentration of 1,2-DP in all runs was 6.8×10^{-3} M unless noted otherwise

^bA fourth run gave $1.16 \times 10^{-4} \text{ sec}^{-1}$

^cThe concentrations of 1,2-DP in these runs were 3.4×10^{-3} M, 5.2×10^{-3} M, and 6.8×10^{-3} M respectively.

^dThis run was followed through its developing acidity. The 1,2-DP disappeared completely within a few minutes. This reaction is too rapid to be followed by this method.

is evidently that of fluorosilicates and fluoroborates formed by the action of HF on glass. Thus the "missing" fluoride in the kinetic runs, fortuitously corresponding to about one equivalent of HF, was lost in the reaction of the liberated HF with the walls of the glass reaction vessel. Indeed, it was noted that the flask used for these runs had, after several runs, become just visibly etched. (Note: The concentration of HF in these experiments was rather low, about 0.01 molar.)

Experiments were conducted in polyethylene and FEP-fluorocarbon bottles in which weighed quantities of 1,2-DP in 90% water-10% dioxane were heated at 50° for about ten half-lives. The results for liberated fluoride ion were erratic, and the bottles seemed to become slowly conditioned with repeated runs. Even with bottles preconditioned to HF, the best value obtained was 2.6 equivalents of HF per equivalent of 1,2-DP.

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The reaction of HF with glass should offer no difficulty to the kinetics. It is expected that perhaps small corrections will have to be made on the results in Table XIII and all subsequent results. The gross features of the data, of course, will remain unchanged.

b. 2,2-DP--Similar studies were carried out on 2,2-DP. It was found, however, that this isomer is stable under these conditions. Thus, no fluoride was liberated in experiments in which 2,2-DP was heated at 50° for several days in 90% water-10% dioxane. Solutions of the 2,2 isomer containing 2 M KF and 2 M KOH remained unchanged over several days at 50°, and the 2,2 isomer was recovered unchanged. In contrast, similar solutions containing the 1,2 or 1,3 isomer become colored after a matter of minutes and none of the reactants could be recovered.

c. 1,3-DP--Preliminary experiments with the 1,3 isomer show that at 50° in 90% water-10% dioxane decomposition occurs more slowly than with 1,2-DP. The resulting solutions are acidic and yield no identifiable products. Malononitrile, $\text{CH}_2(\text{CN})_2$, would be the expected product; traces of it were found in the thermal studies. However, $\text{CH}_2(\text{CN})_2$ can easily undergo any of a number of condensation and hydrolysis reactions under acidic conditions. Thus its isolation from such conditions is not very likely.

3. Promotion of the Decomposition by Various Bases

Both 1,2-DP and 1,3-DP are readily dehydrofluorinated by a variety of bases. Among them are triethylamine, pyridine, and sodium acetate. NFP was isolated from the 1,2 isomer. However, no identifiable products were derived from the 1,3 isomer.

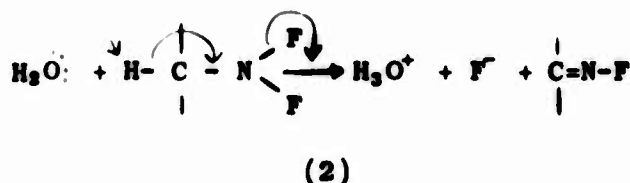
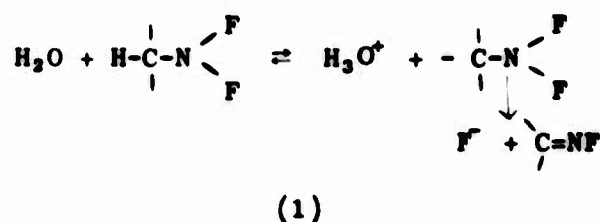
4. Discussion of the Mechanism

The decomposition of NF_2 compounds at higher temperatures in aprotic solvents is probably a surface-catalyzed decomposition. In water-dioxane, however, the ease with which dehydrofluorination occurs implies some solvent participation. The absence of acid catalysis suggests that water is probably acting as a base in promoting the elimination. The ready

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promotion of the elimination process by the addition of KF is explained by the fact that an aqueous solution of a fluoride salt is slightly basic (pH ~ 9) due to hydrolysis of the fluoride to HF. And, as previously stated, the elimination is promoted by base.

There are two courses of reaction traditionally proposed for simple elimination of this type. The substrate may either rapidly and reversibly lose a proton and then slowly liberate fluoride ion (mechanism 1), or the substrate may lose HF in a concerted process (mechanism 2). While (2) is followed in the majority of eliminations, (1) is followed by some compounds in which there are strongly electron-withdrawing groups.²⁵



It is thus conceivable that the elimination here proceeds through the carbanion mechanism, (1), due to the highly electronegative NF₂ groups.

To determine which path was followed in these decompositions, sodium acetate and 1,2-DP were dissolved in CH₃OD, and the mass spectrum taken after about half of the 1,2-DP had disappeared. There was no incorporation of deuterium into the unreacted 1,2-DP. Thus, the concerted process, (2) is the one followed.

The decomposition of 1,2-DP in nitrobenzene could follow a variety of routes. The fact that there is no acid catalysis in an aqueous

²⁵ J. Hine, R. Wiesboeck, R. G. Shirardelli, J. Am. Chem. Soc. 83, 1219 (1961).

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medium does not rule out such a scheme operating in a nonprotic media. However, general base catalysis is just as likely. We cannot at this time draw any definite conclusions concerning the decomposition under these conditions.

The decomposition in methanol is accelerated by added salts and acids probably because these materials increase the ionic strength of the medium.

5. Future Work

Rates of decomposition of several more NF_3 compounds will be obtained. Products will be isolated and identified whenever possible. A confirmation of the role of water in the decomposition will be made.

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VII PROGRAM ORGANIZATION

This project is the responsibility of the Propulsion Sciences Division in cooperation with the Pculter Research Laboratories and the Chemical Physics Division. Project organization and principal contributors to the technical work follow:

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Adaptation of JANAF Test:	J. A. Neff D. B. Moore A. B. Amster R. W. McLeod
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Kinetics and Mechanisms of Thermal Decomposition:	T. Mill D. S. Ross M. M. Smart M. E. Hill

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APPENDIX A

Adaptation of the JANAF Booster Test: Data Reduction

(A. B. Amster, J. A. Neff)

The equation for reducing the data from the witness plates is derived as follows:

Assume the following:

1. There is a small, finite, but reproducible time for a detonation to propagate across explosive interfaces. This is frequently referred to as an "induction time."
2. The time required for two detonations which originate at a common point and meet at a point x is the same for two corresponding paths.
3. The detonation velocity of explosives is a reproducible function of environment.

Our notation is as follows:

P = lengths of MDF, the subscript denotes the particular branch

P_0 = length of MDF from tetryl booster that initiates the explosive on witness plate

V = detonation velocity of any P with corresponding subscript

V_s = wave velocity within sample

V_w = detonation velocity of standard explosive used

L = distance between opposing points of initiation for each sheet explosive finger

x = point at which detonations meet; measured from MDF

ds' = distances between MDF on sample cup

dw' = distances between corresponding strips of explosive on witness plate

ds = distance from tetryl pellet to first MDF

dw = distance from the start to strip 1 on witness plate

τ, τ_1 = small, unknown, but reproducible delay or induction times in transition from cup to MDF and MDF to EL-506-D.

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The time required for the detonation to travel from the tetryl through the sample cup, the first "finger" of MDF and to point x_1 in the sheet explosive is:

$$t_1 = \frac{ds}{V_s} + \mu + \frac{P_1}{V_1} + \eta + \frac{x_1}{V_w} \quad (1)$$

The time required for the detonation to travel from the tetryl through the "start" branch of the MDF and to x_1 through the sheet explosive from the opposite direction is:

$$t_1' = \frac{P_0}{V_0} + \eta + \frac{dw}{V_w} + \frac{L-x_1}{V_w} \quad (2)$$

Equating (1) and (2) and rearranging terms:

$$\frac{ds}{V_s} = \frac{P_0}{V_0} - \frac{P_1}{V_1} + \frac{dw}{V_w} + \frac{L-2x_1}{V_w} - \mu \quad (3)$$

Similarly, by equating the times of travel from the tetryl to point x_2 in the second finger of sheet explosive:

$$\frac{ds + ds'}{V_s} = \frac{P_0}{V_0} - \frac{P_2}{V_2} + \frac{dw + dw'}{V_w} + \frac{L-2x_2}{V_w} - \mu \quad (4)$$

Subtracting (3) from (4) and noting that $P_1 = P_2$ and $V_1 = V_2$:

$$\frac{V_s}{V_w} = \frac{ds'}{dw' + 2(x_1 - x_2)} \quad (5)$$

V_w , ds' , dw' are conditions of the experiment; x_1 and x_2 are measured; therefore V_s can be calculated.

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APPENDIX B

A Thermistor as a Combination Liquid Level and Temperature Sensor

(Donald Baker Moore)

Experiments which involve remote handling of hazardous condensable gases such as modern monopropellants often require temperature monitoring and positive indication that condensed liquids have reached certain container levels. The simplest systems, including sight glasses and floats, may be unsuitable because of potential explosion or other personnel hazards. More sophisticated methods, including acoustic or electrical resonance measurements, optical refraction, or nuclear means, may be unnecessarily complex or the probe-sensing element may be too expensive for a potentially expendable system. Such devices also require an additional temperature-measuring probe which is often a thermocouple. A thermocouple alone is frequently inadequate since the saturated vapor and condensate often may be at the same temperature.

A thermistor element such as the VECO 32A11 (Victory Engineering Co., Springfield, New Jersey) is used in this laboratory to combine these measurements with one inexpensive probe. A small, measured direct current in the range of one to ten milliamperes is passed through a thermistor sealed into the experimental chamber at the desired level. The potential drop across the thermistor is measured. This yields both the resistance and power dissipated in the device. The resistance is compared with the thermistor specifications to find the internal temperature of the probe. This temperature is then plotted against the power dissipation figure. A second measurement at a different input current designates a second point on the graph. A straight line through these points intercepts the axis of zero power dissipation at a value corresponding to the temperature of the probe environment. The slope of this line (or its reciprocal) in milliwatts per degree measures the thermal conductivity of the probe environment. This will usually be found to vary by an appreciable factor between the liquid and gas states, and will be characteristic of the sample material.

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Figure B-1 shows some test data on this system using Freon 12 as a sample gas. In this case the thermal conductivity changes by nearly a factor of four as the probe environment changes from gas to liquid.

This system is useful at probe temperatures up to 300°C and has been used in liquids at -80°C, although at very low temperatures some care may be required to keep the thermistor's internal temperature above that of its environment to prevent its resistance from becoming impractically large.

The measurements are most conveniently made with a measured or constant current supply and a potentiometric voltage recorder. The thermal time constant for the usual thermistor varies from one or two seconds in a liquid to approximately twenty-five in a gas, so while the indication is not continuous it can be relatively rapid. Obviously, reduction of the observations can be facilitated by suitable graphs.

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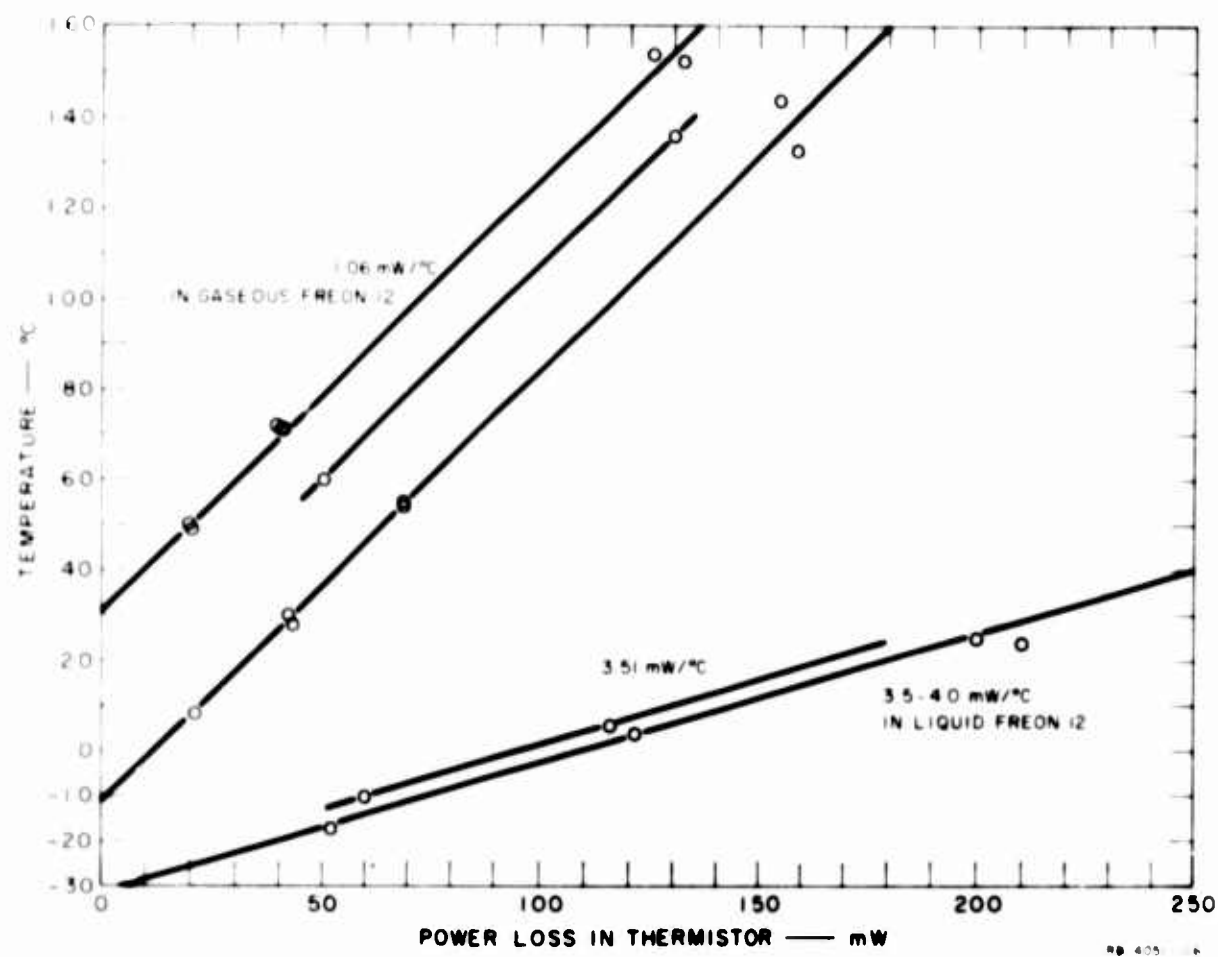


FIG. A-1 POWER LOSS IN THERMISTOR VERSUS TEMPERATURE

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13 ABSTRACT Under the sponsorship of ARPA and the Office of Naval Research, Stanford Research Institute is studying fundamental sensitivity properties of difluoroamino compounds in the following situations. <ol style="list-style-type: none">1. The detonation characteristics including the shock sensitivity of the liquid phase2. The relation of shock sensitivity and failure diameter to the flow and the chemical reaction rate behind the shock front3. The mechanism and kinetics of thermal decomposition of the compounds in solution and in the liquid phase. <p>These interrelated situations were chosen for their susceptibility to analysis in terms of basic physical and chemical parameters. Each study is being carried out on 1,2-bis(difluoroamino)propane (1,2-DP) and 2,2-bis(difluoroamino)propane (2,2-DP), in order to assess the importance of structural variation. Thermal decomposition studies have also begun on 1,3-bis(difluoroamino)propane (1,3-DP).</p> <p>A. <u>Detonation Sensitivity.</u> The shock sensitivities of 2,2-DP and IBA have been measured. The 2,2-DP sensitivity was found to be 13.2 ± 0.5 mm of Plexiglas in lead cups (9.5 mm I.D. x 2 mm wall). The IBA sensitivity was measured in lead cups (20 mm I.D. x 2 mm wall) and found to be 14.4 ± 0.2 mm of Plexiglas. The effect of the detonation sensor, a continuous wire mounted in a holder, was</p> <p style="text-align: right;">(Cont'd.)</p>			

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Sensitivity of NF Compounds Thermal decomposition kinetics Detonation sensitivity Failure Diameter Low velocity waves Modified JANAF test Perfluorohydrazine Detonation velocity						

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13. ABSTRACT (cont'd.)

investigated. It was concluded that a wire reaching to the donor-acceptor interface can cause an apparent increase in sensitivity, but a wire reaching halfway into the test liquid does not affect the sensitivity for the charge length used. From streak camera photographs of the sensitivity test, it appears that initiation occurs at the tube walls. There may also be an initiation effect, as yet unexplained, caused by the type of material which seals the test cup bottom. The donor-attenuator calibration has been checked and a large amount of scatter was noted, probably caused by irreproducibility of the donor components.

B. Low Velocity Reaction Waves. Low velocity reaction waves have been observed in a mixture of 90% (by weight) nitromethane - 10% tetranitromethane in steel tubes 25.4 mm I.D. x 6.35 mm wall. The average velocity in the liquid is 1.5 mm/ μ sec and the average recorded shock pressure about 13 kbars. By observing this mixture in sample containers of CR-39 and of aluminum, steel, and lead, all equipped with windows made of CR-39, the precursor wave in the sample container walls and the slower reaction wave in the liquid mixture has been seen. The average velocity in the liquid is 1.5 ± 0.4 mm/ μ sec and is independent of container material.

C. Detonation at Low Temperatures. Two methods for determining the detonation velocity have been successfully adapted to distinguish between detonating and nondetonating phenomena at cryogenic temperatures. The methods are (1) the modified Dautriche method which compares the detonation velocity of a known explosive with that of the test material, and (2) the continuous resistance wire method. Both methods confirm that liquid perfluorohydrazine does not detonate under the test conditions.

D. Failure Diameter and Reaction Time. The failure diameter for a Chapman-Jouguet detonation wave in 1,2-DP in massive lead confinement is between 1.6 and 2.0 mm. Failure diameter determinations for 2,2-DP and IBA are partially completed. The detonation velocity of 1,2-DP was measured as 5.89 ± 0.05 mm/ μ sec at 37°C with the liquid confined in a 25 mm I.D. by 6.3 mm CR-39 plastic tube. Hugoniot curves are being determined for Plexiglas, CR-39, nitromethane, and difluoroamino compounds. Preliminary measurements have been made of the reaction time of nitromethane as a function of Plexiglas attenuator thickness. Methods for the measurement of reaction time in difluoroamino compounds are being refined.

E. Low Pressure Pyrolysis. The thermal decomposition of 1,2-DP and 2,2-DP has been studied by passage of small quantities of the compounds into a heated quartz vessel at pressures so low that only gas-wall collisions occur. Products emerging by diffusion were analyzed by a mass spectrometer. Results of preliminary observations of 1,2-DP and 2,2-DP decomposed at 600-900°C show that (a) 2,2-DP decomposes faster than 1,2-DP in our system; (b) decomposition of 1,2-DP gives as one of the major reaction paths: $C_2H_5 + 2NF_2$; (c) most of the main features of the 1,2-DP decomposition can be accounted for by assuming an initial NF_2 split out, followed by rearrangement; (d) under these conditions there seems to be no need to propose a homogeneous NF elimination for either 1,2-DP or 2,2-DP; and (e) there is no evidence for catalytic decomposition of either compound on the quartz walls.

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13. ABSTRACT (cont'd.)

F. Decomposition of NF Compounds in Solution. Early studies suggested that the thermal decomposition of NF compounds proceeded through a dehydrofluorination catalyzed by acid, base, or both. Studies during this report period in 10% dioxane-water at 50° with 1,2-DP show that there is no acceleration of decomposition by addition of HCl and thus, at least under these conditions no acid catalysis. The dehydrofluorination of NF compounds is most likely promoted by water, acting as a base in the elimination reaction. Experiments in methanol-d show that the elimination is probably a concerted one.

Studies with 2,2-DP indicate that for these same conditions it is completely stable. The 1,3 isomer, from a qualitative study, decomposes more slowly than does 1,2-DP. Furthermore 1,2-DP and 1,3-DP readily undergo dehydrofluorination in the presence of base.

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